PHOTOELECTRON SPECTROSCOPY OF ALKYL AND ALKENYL FREE RADICALS

Thesis by

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To Mom and Dad

Acknowledgments

I heartily thank Jack Beauchamp for his encouragement and advice. Thanks also go to all the members of the Beauchamp group who have so often lent an ear, given some help and offered their ideas. The members of the Caltech shops have been very helpful. Sharon ViGario cheerfully and expertly typed this thesis.

I thank my parents and my husband, Pete, for their enduring love, encouragement and support. Much appreciated were the times, especially when experiments were not working, when Pete made me laugh.

Abstract

The first bands of the photoelectron spectra of simple alkyl and alkenyl free radicals, produced by pyrolysis of organic nitrites, are presented. Thermochemical and structural information about the corresponding carbocations in the gas phase are obtained from interpreting the spectra. In particular, adiabatic ionization potentials are combined with radical heats of formation to obtain heats of formation of the cations. The photoelectron band shapes are discussed in terms of structural changes occurring upon ionization. The focus of this work is the study of isomeric radicals. Their photoelectron spectra allow the characterization of a series of carbocations with well-defined structures, namely those which closely resemble the radicals, even when the cations can rearrange with little or no activation energy to more stable forms. Radical thermal rearrangement and decomposition pathways are also studied.

Chapter I provides a brief introduction to the field of photoelectron spectroscopy of transient species, including a compilation of photoelectron data of transient species, and an introduction to the specific work presented in this thesis. Chapter II presents the photoelectron spectra of the C_4H_7 radicals 1-methylallyl, 2-methylallyl, allylcarbinyl and cyclobutyl radical, which provide information about the corresponding $C_4H_7^+$ carbocations in the gas phase. These cations are of long-standing interest in the cyclopropylcarbinyl, cyclobutyl and allylcarbinyl interconversions observed in solvolysis reactions. The photoelectron spectra of 1-propyl, 1-butyl, isobutyl, neopentyl and 2-butyl radicals are presented in Chapter III. The corresponding primary cations are of particular interest because they are often postulated as intermediates or transition states in gas-phase and solution isomer-

ization processes.

Chapter IV describes the application of photoelectron spectroscopy to the study of low-pressure gas-surface reactions. Organic radicals, as well as stable products, have been detected directly after exiting the catalyst bed. Allylic hydrogen abstraction by heated bismuth oxide catalyst forms gas-phase allyl and 2-methylallyl radicals from propylene and isobutylene in the presence of oxygen. Mechanistic information is obtained by varying the catalyst temperature and reactant partial pressures.

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CHAPTER I

Introduction

Less than a decade after the development of ultraviolet photoelectron spectroscopy (PES) of gas-phase molecular species[1-4], the photoelectron spectra of the first transient species studied were published by Jonathan and co-workers in 1970[5,6]. They reported the spectra of atoms and excited diatomics produced in a microwave discharge. Since then the area of photoelectron spectroscopy of transients has become an increasingly active field of research[7]. The types of transient species that have been studied include free radicals, atoms, intermolecular complexes, excited molecules, negative ions and closed-shell reactive molecules. Temperature-dependent equilibria and nonvolatile compounds which have appreciable vapor pressure only at high temperatures have also been investigated.

Photoelectron spectroscopy yields information about the electronic structure of the neutral and the ion. Adiabatic ionization potentials provide heats of formation of the ion in specific electronic states relative to the ground state of the neutral. Since Franck-Condon factors govern the photoionization process, photoelectron band shapes and resolved vibrational structure reflect the geometry changes occurring upon ionization. Their analysis can yield the bonding character of the orbital from which the electron was removed. In addition, photoelectron spectroscopic studies of transient species can provide insight into the reactions involved in generating the transient and its subsequent decomposition or reaction by identifying other products present in the gas phase reaction mixture.

To illustrate the extent of the work done, Tables I-IV[8] present an updated summary of the photoelectron data for transients, initially

Table I. Photoelectron data for open- and closed-shell organic transient molecules[a].

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
Open Shell					
$H\dot{C}O$	MWD[b], reaction F + H_2CO	8.27[c,d]	9.31	760	10
$D\dot{C}O$	MWD, reaction F + D_2CO	8.26[c]	9.23	620	10
$F\dot{C}O$	MWD, reaction F + HFCO	8.76[c]	11.26	650	11
$CH_3\cdot$	Pyrolysis	9.82	9.82	720,2720	12
	$CH_3N{=}NCH_3$	9.84[d]	9.84	1380	13,14
$CD_3\cdot$	Pyrolysis	9.83[d]	9.83	1050	13
	$CD_3N{=}NCD_3$				
$CH_3\dot{C}H_2$	Pyrolysis	8.39	8.51	--	14
	$CH_3CH_2CH_2ONO$				
	MWD, reaction F + CH_3CH_3	8.32	8.53	370	7a
$CH_3\dot{C}D_2$	Pyrolysis	8.38	8.50	--	14
	$CH_3CD_2CH_2ONO$				

Table I (continued)

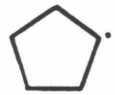
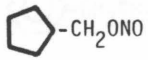
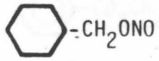
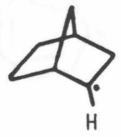
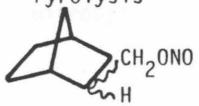
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
$CH_3\dot{C}HCH_3$	Pyrolysis $(CH_3)_2CHCH_2ONO$	7.36	7.69	730,970	14
$\cdot C(CH_3)_3$	Pyrolysis	--	6.95	410,800	12
	t-bu-N_2-t-bu	6.58[d,e]	6.90	460,760	15
	Pyrolysis $(CH_3)_3CCH_2ONO$	6.70	6.92	450	14
$(CH_3)_2\dot{C}$-C≡N	Pyrolysis AIBN	--	8.56	--	16
	Pyrolysis	7.21	7.46	--	17,18
					
	Pyrolysis	7.15	7.40	--	17,18
					
	Pyrolysis	6.84	6.84	--	18
					

Table I (continued)

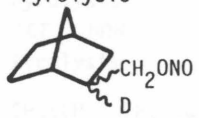
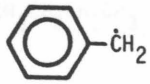
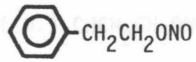
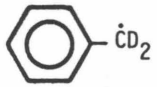
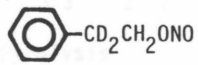
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
	Pyrolysis 	6.83	6.83	--	18
$CH_2{=}C\dot{H}CH_2$	Pyrolysis $CH_2{=}CHCH_2CH_2ONO$	8.13	8.13	420	19
	Pyrolysis bibenzyl	7.43[d]	7.43	--	16
	Pyrolysis 	7.20[d]	7.20	560	19
	Pyrolysis 	7.22[d]	7.22	480	19
	Pyrolysis bitropyl	6.28[d]	6.28	1420	20

Table I (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
$(CF_3)_2NO\cdot$	Pyrolysis $(CF_3)_2NOH$	--	10.7[d]	--	21
$CH_3CH_2\dot{C}H_2$	Pyrolysis $CH_3(CH_2)_2CH_2ONO$	8.15	8.43	540	22
$CH_3CH_2CH_2\dot{C}H_2$	Pyrolysis $CH_3(CH_2)_3CH_2ONO$	8.02	8.50	--	22
$CH_3CH_2\dot{C}H_2CH_3$	Pyrolysis $CH_3CH_2CH(CH_3)CH_2ONO$	7.25	7.59	--	22
$(CH_3)_2CH\dot{C}H_2$	Pyrolysis $(CH_3)_2CHCH_2CH_2ONO$	7.93	8.31	--	22
$(CH_3)_3C\dot{C}H_2$	Pyrolysis $(CH_3)_3CHCH_2CH_2ONO$	7.88	8.25	--	22
$CH_2=CHCH_2\dot{C}H_2$	Pyrolysis $CH_2=CH(CH_2)_2CH_2ONO$	8.04	8.47	--	23

Table I (continued)

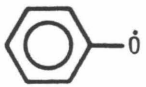
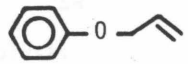
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
$CH_2=CH\dot{C}HCH_3$	Pyrolysis $CH_2=CHCH(CH_3)CH_2ONO$	7.49[f]	7.67	Observed	23
$CH_2=C(CH_3)\dot{C}H_2$	Pyrolysis $CH_2=C(CH_3)CH_2CH_2ONO$	7.90	7.95	410	23
	Pyrolysis 	7.54	7.66	990	23
$\cdot CH_2Cl$	MWD, reaction F + CH_3Cl	8.75	8.88	1020	24
$\cdot CH_2Br$	MWD, reaction F + CH_3Br	--	8.75	870	24
	Pyrolysis 	8.56[d]	8.56	--	25

Table I (continued)

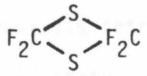
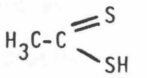
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
Closed Shell					
H_2CS	Pyrolysis	9.34[d]	9.34	1000	26
	CH_3SSCH_3				
	Pyrolysis	9.38[d]	9.38	935	27
	CH_3SCl				
F_2CS	Pyrolysis	10.45[d]	10.62	1380,450	28
					
CHClO	Reaction	11.51[d]	11.61	610,830,1390	29
	$HCOOH + PCl_5$				
$H_2C=C=S$	Pyrolysis	8.89[d]	8.89	1450,700	30
					
H_2CSO	Pyrolysis	?	10.23[d]	?	31
					

Table I (continued)

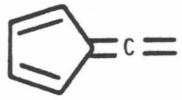
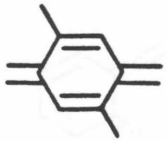
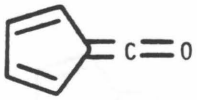
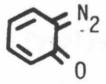
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
CF_2	MWD C_2F_4	11.42[d,e]	12.24	650	32
	Pyrolysis phtalide	8.22[d]	8.22	?	33
	Pyrolysis [2.2]paracyclophane	7.87[d]	7.87	?	34
	Pyrolysis tetramethyl [2.2]paracyclophane	7.58[d]	7.58	?	35
	Pyrolysis tri-tert-butylcyclopentadienone	--	6.83	?	36
	Pyrolysis 	--	8.56[d]	?	37

Table I (continued)

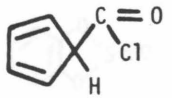
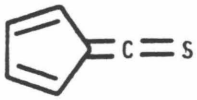
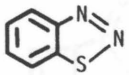
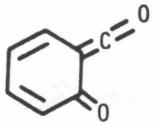
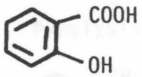
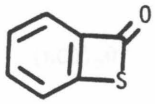
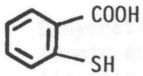
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
	Pyrolysis 	--	8.39[d]	?	38
	Pyrolysis 	--	8.52[d]	--	37
	Pyrolysis 	--	8.43[d]	--	37
	Pyrolysis 	--	8.56[d]	--	37
	Pyrolysis orthoquinone	--	9.49[d]	1200	39

Table I (continued)

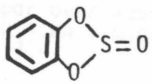
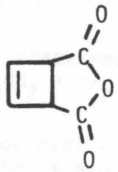
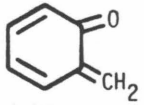
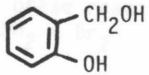
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
	Pyrolysis	--	9.41[d]	?	40
	 or				
	 or 				
	Pyrolysis	8.80[d]	8.80	?	41
					
$(HCO)_2O$	Dehydration of formic acid (in-situ or not)	--	11.32[d]	--	42
		--	11.34[d]	--	43
CH_3NHCl	Vapor over aqueous CH_3NH_2 + NaOCl	9.19[d]	9.80	--	44

Table I (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
CH_3NCl_2	Vapor over aqueous CH_3NH_2 + NaOCl	9.35[d]	10.01	--	44
$(CH_3)_2NCl$	Vapor over aqueous $(CH_3)_2NH$ + NaOCl	8.67[d]	9.31	--	44
CH_3NHBr	Vapor over aqueous CH_3NH_2 + NaOBr	9.12[d]	9.60	--	45
	Gas phase reaction CH_3NH_2 + Br_2	--	9.67[d]	--	46
CH_3NBr_2	Vapor over aqueous CH_3NH_2 + NaOBr	9.15[d]	9.62	--	45
	Gas phase reaction CH_3NH_2 + Br_2	--	9.68[d]	--	46
$(CH_3)_2NBr$	Vapor over aqueous CH_3NH_2 + NaOBr	8.61[d]	9.14	--	45
CH_2=NH	Pyrolysis CH_3NH_2	~10.0[d]	10.52	--	47
	Pyrolysis H_3CN_3	--	10.70[d]	--	48

Table I (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
	MWD	--	10.55[d]	--	49
	CH_3NH_2				
	Pyrolysis	--	10.56[d]	--	50
					
$CH_2=NCH_3$	Pyrolysis	--	9.90[d]	--	51
	N-trimethylhexahydro-s-triazine				
$CH_3CH=NH$	Pyrolysis	?	10.18[d]	--	51
	c-trimethylhexahydro-s-triazine				
$CH_3N=NH$	MWD	8.8[d]	9.57	--	52
	CH_3NHNH_2				
$CH_2=CHCH=NH$	Pyrolysis	--	10.2[d]	--	50
	$(CH_2=CHCH_2)_2NH$				

Table I (continued)

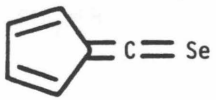
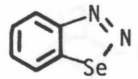
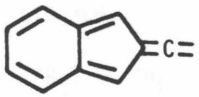
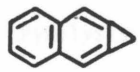
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
$Cl_2C=C=O$	Cl_3CCOCl over heated Zn	9.07[d]	9.07	330,1100	53
	Cl_3CCOBr over heated Zn	--	9.15[d]	?	38
$CH_3CH=C=C=O$	Pyrolysis				
	$CH_3CH=CHCCl=O$	--	8.9[d]	--	38
$H_2C=C=Se$	Pyrolysis	8.72[d]	8.72	1300	54
		8.7[d]	8.7	1450	55
	Pyrolysis	--	8.34[d]	--	54
					
	Pyrolysis	--	7.25[d]	?	56
					

Table I (continued)

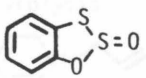
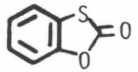
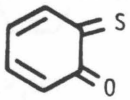
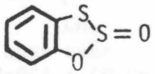
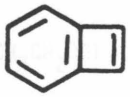
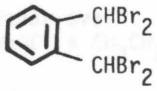
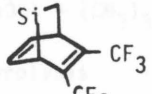
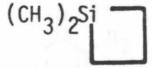
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
	Pyrolysis  or 	--	8.87[d]	--	57
	Pyrolysis 	?	8.85[d]	?	57
	Pyrolysis  over Mg	--	7.87[d]	--	58
$SiH_2{=}CH_2$	Pyrolysis 	--	--	1010,840,620,200	59
$SiD_2{=}CH_2$	?	?	?	770,550,120	59
$(CH_3)_2Si{=}CH_2$	Pyrolysis	7.71[g]	7.98	760	60
		8.00	8.30	--	61

Table I (continued)

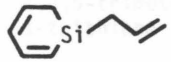
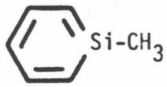
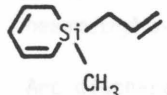
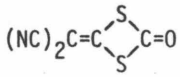
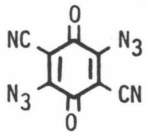
Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
	Pyrolysis 	--	8.0[d]	--	62
	Pyrolysis 	--	7.7[d]	--	63
CH_3OCl	Vapor over $NaOCl + CH_3OH$	10.39[d]	10.48	710	64
CH_3CH_2OCl	Vapor over $NaOCl + CH_3CH_2OH$	10.13[d]	10.22	720	64
$(CH_3)_3COCl$	Vapor over $NaOCl + (CH_3)_3COH$	--	9.91[d]	--	64
$(NC)_2C=C=S$	Pyrolysis 	--	9.94[d]	1500	65
$(NC)_2C=C=O$	Pyrolysis 	--	10.56[d]	1150	66

Table I (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
CH_3HCS	Pyrolysis 1,3,5-trimethyl s-trithiane	8.98[d]	8.98	950	67
$(CH_3)_2CS$	Pyrolysis hexamethyl s-trithiane	8.60[d]	8.60	--	67
HC≡P	Arc discharge phosphine; kept at -160° C while evaporated into spectrometer	10.79[d]	10.79	1110	68
$CH_3C{\equiv}P$	Pyrolysis $CH_3CH_2PCl_2$	9.89[d]	9.89	1420	69
FC≡P	CF_3PH_2 over KOH	10.37[d]	10.57	1725,760	70

Table I (continued)

Footnotes

[a]The following key was observed as closely as possible:
A-- for an IP means a value can be estimated from the spectrum presented, but no value was reported;
a ? means no spectrum is given from which an IP could be estimated. A ? for an adiabatic IP may mean the band onset is obscured. A -- for vibrational structure means the band is without structure; a ? means the spectrum presented displays distinct structure but no frequency is reported.

[b]MWD = microwave discharge.

[c]Calculated from a Franck-Condon analysis of the first PES band. The band onset is at 8.55 eV for HCO, 8.56 eV for DCO and 10.47 eV for FCO.

[d]Higher IP's of the transient were identified.

[e]Hot bands may contribute significantly to this spectrum.

[f]The PES band arises from ionization of both the cis- and trans-1-methylallyl radical. The adiabatic IP is assigned to the trans isomer.

[g]To be regarded as a lower limit since hot bands cannot be ruled out.

Table II. Photoelectron data for open- and closed-shell inorganic transient molecules and atoms[a].

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
Open Shell					
H	MWD[b] H_2	13.61	--	--	5
N	MWD N_2	13.62	--	--	5
O	MWD O_2	14.55[c]	--	--	5
F	MWD CF_4	17.47[c]	--	--	71
Cl	MWD Cl_2	12.97[c]	--	--	71
Br	MWD Br_2	11.81[c]	--	--	71
I	MWD, reaction $Br + I_2$	10.43[c]	--	--	71
	Laser (argon ion) photolysis I_2	10.45[c]	--	--	72
S	MWD, reaction $F + H_2S$	10.36[c]	--	--	73
OH	MWD, reaction $H + NO_2$	13.01[c]	13.01	2950	74
OD	MWD, reaction $D + NO_2$	?	?	2260	74

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
SH	MWD, reaction $F + H_2S$	10.37[c]	10.37	2450	73
SD	MWD, reaction $F + D_2S$	?[c]	?	1740	73
FO	MWD, reaction $F + O_3$	12.77[c]	13.08	1300	75
ClO	MWD, reaction $Cl + O_3$	10.95[c]	11.01	1040	76
	MWD, reaction $Cl + ClO_2$				
BrO	MWD, reaction $O + Br_2$	10.29	10.29	830	77
NS	MWD NSCl	8.87	8.87	1415	78
	Pyrolysis S_7NH				
SO	MWD SO_2	10.29[c]	10.29	1360	79
S_2	Heating flowers of sulfur	9.38[c]	9.38	770	80

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
PO	MWD/Pyrolysis reaction O + P_2	8.39	8.39	1410	81
ClO_2	?	10.37[c]	10.5	1014,520	21
NF_2	Pyrolysis N_2F_4	11.63[c]	12.1	1250	21
SO_3F	Pyrolysis $S_2O_6F_2$	12.85[c]	12.85	1220	21
N_3	MWD, reaction F + HN_3	11.06[c]	11.06	1170,2565	82
NH_2	MWD, reaction F + NH_3	11.46[c]	12.00	840	83
DH_2	MWD, reaction F + ND_3	11.45[c]	12.01	660	83
HO_2	MWD, reaction F + H_2O_2	11.35	11.54	1560	84
DO_2	MWD, reaction F + D_2O_2	11.35	11.54	1595	84

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
PF_2	MWD, reaction F + PH_3	?	?	1000	7a
SiH_3	MWD, reaction F + SiH_4	8.14	8.74	820	85

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
Closed Shell					
CS	MWD CS_2	11.33[c]	11.33	1290	86
		11.33[c]	11.33	1330	87
		11.34[c]	11.34	1380	88
SiO	Heating $(SiO)_x$	11.61[c]	11.61	--	89
GeO	Heating Ge + GeO_2 + Ar/He	11.25[c,d]	11.25	830	90
	Heating GeO	11.25[c,d]	11.25	--	91
GeS	Heating GeS	10.36	10.36	--	91
SnO	Heating SnO_2	9.60[c]	9.98	700	92
SiF_2	Heating SiF_4 over Si	--	11.08[c]	?	93
	Heating CaF_2 + Si	10.78[c]	11.18	350	94
GeF_2	Heating GeS + PbF_2	≈11.65[c]	11.98	--	95
$GeCl_2$	Heating GeS + $PbCl_2$	10.20[c]	10.55	--	96

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
$GeBr_2$	Heating GeS + $PbBr_2$	9.60[c]	10.02	--	96
GeI_2	Heating GeS + PbI_2	--	9.08[c]	--	97
PN	Pyrolysis P_3N_5	11.85[c]	11.85	1200	98
		11.88[c]	11.88	1230	99
P_2	RF induction heating, P_4	10.53[c]	10.61	670	100
TlCl	Vaporization TlCl	9.70[c,e]	10.38[e]	--	101
TlBr	Vaporization TlBr	9.14[c,e]	9.83[e]	--	101
TlI	Vaporization TlI	8.47[c]	8.91	--	100
O_3		12.44[c]	12.75	650	32
		12.53[c]	12.75	630	102
S_2O	SO_2Cl + Ag_2S, or	--	10.52[c]	370	103
	MWD SO_2	10.53[c]	10.59	480	104
NSCl	Pyrolysis $N_3S_3Cl_3$	10.61[c]	10.95	--	105

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
HBS	H_2S over B, heated	11.11[c]	11.23	955	106
FCN	MWD cyanuric fluoride	13.34[c]	13.65	2100	107
Tl_2F_2	Vaporization Tl_2F_2	?	9.96[c]	--	108
HN=NH	MWD N_2H_4	9.59[c]	10.02	1180	52
DN=ND	MWD N_2D_4	9.61[c]	10.10	1020	52
N_2S_2	S_4N_4 over Ag wool	10.41[c]	10.52	470,810	109
HNSO	$Cl_2SO + NH_3$	?	11.60[c]	?	110
NCN_3	BrCN over activated NaN_3	11.00	11.00	1900,1120,800	111
ClN_3	Cl_2 over moist, cool NaN_3	10.20[c]	10.38	730	112
BrN_3	Br_2 over moist, cool NaN_3	10.00[c]	10.08	710	112

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
NCNCO	Pyrolysis AgNCO	11.49	11.75	2130,540	111
ClNCO	Pyrolysis $(ClNCO)_3$	10.72[c]	10.86	1110,600	112
BrNCO	Br_2 over heated AgNCO	10.46[c]	10.46	1110,520	112
INCO	I_2 over heated AgNCO	9.89[c]	9.89	420,2070	112
S_8	Sulfur vapor	?	9.23[c]	--	113
HOCl	Vapor over aqueous Cl_2O	11.12[c]	11.22	830	114
BrF	MWD, reaction Br_2 + F	11.77[c]	11.86	750	115
IF	MWD, reaction ICl + F	10.54[c]	10.62	700	115
SBr_2	MWD, Br over flowers of sulfur	?	9.36[c]	400	116
		--	9.33[c]	--	117
SF_2	MWD, F over flowers of sulfur	10.08[c]	10.31	935	118
SeF_2	MWD, F over Se	--	10.20	780	119

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
$SeCl_2$	MWD, Cl over Se	--	9.52[c]	450	119
	Cl_2 over Se	--	9.50[c]	490	120
Se_2Cl_2	Cl_2 over Se	--	9.81[c]	--	120
$SeBr_2$	MWD, Br over Se	--	9.07[c]	--	119
	Br_2 over Se	--	9.17[c]	--	117
$TeCl_2$	Cl_2 over heated Te	--	8.99[c]	--	121
$TeBr_2$	Br_2 over heated Te	--	8.76[c]	--	121
NH_2Cl	Vapor over aqueous NH_3 + NaOCl	9.85[c]	10.52	760	114
$NHCl_2$	Vapor over aqueous NH_3 + NaOCl	9.98[c]	10.56	--	44
NCl_3	Cl_2 over moist NH_4SO_4	10.12[c]	10.69	--	44
$NHBr_2$	NH_3 + Br_2	--	10.1[c]	--	122
		--	--	--	45

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
NH_2Br	$NH_3 + Br_2$	9.65[c]	10.18	620	123
		9.72[c]	10.18	650	45
HNF_2	Vapor over aqueous $F_2 + (H_2N)_2CO$	11.53[c]	12.38	580	124
DNF_2	Vapor over aqueous (D_2O) $F_2 + (H_2N)_2CO$	?	?	530	124
HBF_2	BF_3 over heated $NaBH_4$	13.60[c]	14.33	--	125
$HBCl_2$	BCl_3 over heated $NaBH_4$	11.91[c]	11.91	860	126
$HBBr_2$	BBr_3 over heated $NaBH_4$	--	10.92[c]	--	126
$BClF_2$	$BCl_3 + BF_3$	--	12.85[c]	--	127
BCl_2F	$BCl_3 + BF_3$	--	12.18[c]	--	127
ClSeCN	Cl_2 over AgSeCN	--	10.19[c]	440	128
BrSeCN	Br_2 over AgSeCN	--	9.99[c]	360	128

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
$(SCN)_2$	Cl_2 or Br_2 over AgSCN	--	11.05[c]	920	129
FSCN	$(SCN)_2$ [from Cl_2 over AgSCN] + F_2	--	10.93[c]	840	130
ClSCN	$(SCN)_2$ [from Cl_2 over AgSCN] + Cl_2	10.45[c]	10.52	570	131
BrSCN	$(SCN)_2$ [from Br_2 over AgSCN] + Br_2	10.26[c]	10.32	450	131
ONCN	Cooled ONCl + AgCN	10.93[c]	11.50	--	132
ClBS	Cl_2S_2 over heated B	10.51[c]	10.68	1375	133
BF	BF_3 over heated B	11.12	11.12	1765	134
PF	MWD, reaction F + PH_3	?	9.74	1030	7a
$CrCl_2$	Heating Cr powder + AgCl	--	9.9[c]	--	135
$CrBr_2$	Heating Cr powder + AgBr	--	9.3[c]	--	135

Table II (continued)

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
MnF_2	Heating MnF_2	--	11.82[c]	--	136
$MnBr_2$	Heating $MnBr_2$	--	10.43[c]	--	136
$LaCl_3$	Heating $LaCl_3$	--	11.37[c]	--	137
$LaBr_3$	Heating $LaBr_3$	--	10.68[c]	--	137
LaI_3	Heating LaI_3	--	9.62[c]	--	137

Table II (continued)

Footnotes

[a]For molecules, the following key was observed as closely as possible:
A -- for an IP means a value can estimated from the spectrum presented, but no value was reported; a ? means no spectrum is given from which an IP could be estimated. A ? for an adiabatic IP may mean the band onset is obscured. A -- for vibrational structure means the band is without structure; a ? means the spectrum presented displays distinct structure but no frequency is reported.

[b]MWD = microwave discharge.

[c]Higher IP's of the transient species were identified.

[d]This is the ionization to the (assigned) $\tilde{X}$ state of the ion. In both studies seemingly similar low intensity peaks were observed at lower IP's. Colbourn et al. concluded that these corresponded to ionization to the $\tilde{A}$ state of the ion. White et al. assigned these features to hot bands.

[e]The IP's are the lowest of this species but correspond to formation of the first excited state of the ion. The ground state is a sharp band imbedded in the broad band arising from the excited state.

[f]By comparison with calculations, it was determined that the first band was obscured by the spectra of other species. Higher IP's were identified.

Table III. Photoelectron data for excited molecules.

Species	State(s)	Source	Reference
O_2^*	$^1\Delta_g, ^3\Sigma_g^-$	MWD[a] O_2	6,138,139
$N_2^\dagger$	v" = 0 - 7	MWD N_2	140
$H_2^\dagger$	v" = 0 - 2	MWD H_2	140
$Cl_2^\dagger$	v" = 0 - 2	Heating Cl_2 to 120 °C	141
$O_2^\dagger$	v" = 0 - 1	Heating O_2 to 512 °C	141
Br^*	$^2P_{3/2}, ^2P_{1/2}$	MWD, reaction F + HBr/DBr	7a
Ga^*	$^2P_{3/2}, ^2P_{1/2}$	Heating Ga to 1720 K into flowing He	142

[a]MWD = microwave discharge

Table IV. Photoelectron data for intermolecular complexes[a].

Species	Source	IP(eV) A	IP(eV) V	Vibrational Structure (cm^{-1})	Reference
Ar_2	Supersonic expansion Ar	14.44[b,c]	15.55	--	143
$(CH_3OH)_2$	Supersonic expansion CH_3OH	$\leq$9.8[c]	10.42	--	144
$(CH_3)_2O \cdot BF_3$	Sampling $(CH_3)_2O + BF_3$ (10 torr) through nozzle	--	12.02[c]	--	145
	Sampling $(CH_3)_2O + BF_3$ (3 torr) through nozzle; fast cryopumping in ionization region	--	12.4[c]	--	146
$(CH_3)_2O \cdot HF$	Sampling $(CH_3)_2O + HF$ (0.2 - 0.8 atm) through pinhole	--	11.04[c]	--	147
$(NO_2)_2$	Cold (-30 to -50 °C) NO_2 gas or vapors from frozen N_2O_4	--	11.4[c]	--	148
	Sampling high pressure (~ 1 atm) NO_2	--	11.6[c]	--	149
		--	11.45[c]	--	150
		--	11.4[c]	--	151

Table IV (continued)

Footnotes

[a]The following key was observed as closely as possible:
A -- for an IP means a value can be estimated from the spectrum presented, but no value was reported;
a ? means no spectrum is given from which an IP could be estimated. A ? for an adiabatic IP may mean the band onset is obscured. A -- for vibrational structure means the band is without structure;
a ? means the spectrum presented displays distinct structure but no frequency is reported.

[b]Calculated from Ar_2^+ dissociation energy. Not observed because of an exceedingly low Franck-Condon factor for the 0-0 transition.

[c]Higher IP's were identified.

compiled by F. A. Houle[9]. Precursors, methods of generation, first ionization potentials and observed vibrational structure on the first photoelectron bands are listed[5,6,7a,10-15]. This compilation of neutral transients is as complete as possible, except for intermolecular complexes and those inorganic molecules and atoms produced by high-temperature heating of solids. A representative sampling of the van der Waals, hydrogen-bonded and electron donor-acceptor complexes which have been studied are listed. Only a few of the many inorganic species studied in high-temperature vapors by the major contributors in this field, J. Berkowitz, D. A. Shirley, J. M. Dyke, A. W. Potts, E. P. F. Lee, A. F. Orchard, G. K. Schweitzer and their co-workers, are listed. One is referred to publications by W. C. Lineberger and co-workers for negative ion photodetachment spectra.

A primary challenge in the field of PES of transients is devising an efficient method of generating the species by combining appropriate precursors and techniques. Due to the large overlapping of molecular photoelectron spectra, the transients must be generated in fairly high concentrations. Techniques which have been used include microwave discharge, gas-phase pyrolysis, atom-molecule reactions, gas-solid surface reactions and expansion through a supersonic nozzle. Recent ovens built to produce high-temperature vapors rely on pulsed radiofrequency inductive heating[7c] and radiative heating[152]. Only one transient, atomic iodine, has been produced by laser photolysis[72]. Ideally, this technique has great potential used in conjunction with the conventional photoelectron experiment in which a rare gas lamp photoionizes the transient or used such that the same laser which photodissociates the precursor photoionizes the transient in a multiple photon process.

Recently, benzene was identified by its KrF laser photoelectron spectrum as a product from KrF laser irradiation of benzaldehyde[153]. In the future, transient photochemical products may be detected by this method.

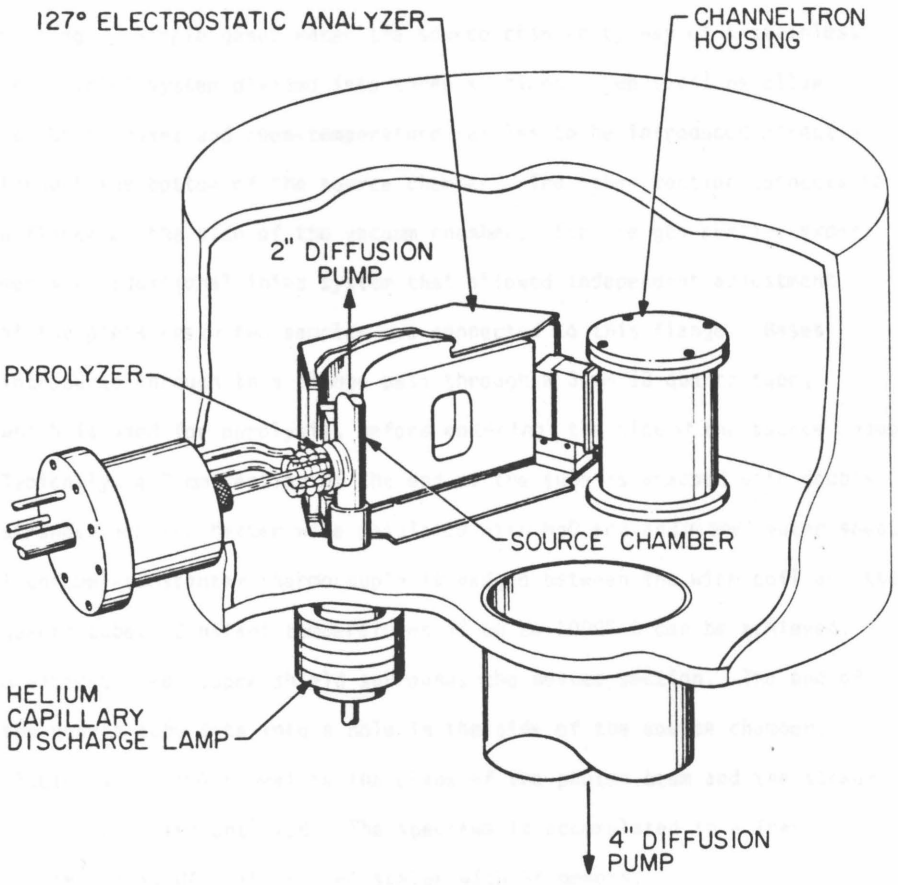
Along with the development of techniques to generate the transients, specially designed spectrometers have been built[7c,49,152,154], and data acquisition and treatment procedures have been implemented to be able to obtain high resolution spectra of transient species with ever-increasing sensitivity and selectivity. Important considerations for the spectrometer are an efficiently pumped photoionization region, in order to minimize the residence time of the transient, and a sampling system which permits freedom in the method of generating the species. To extract the transient signal, square-wave modulation of a microwave discharge, with a modulation depth of 100%, has been used in conjunction with detector gating circuitry[139]. This was combined with a lock procedure which allows multiple scans to be superimposed correctly, avoiding loss of resolution due to spectral drift. Recently, multichannel electron detectors have been used to provide substantial reduction in the time required to obtain the spectrum, minimizing the extent of resolution and signal-to-noise deterioration due to chemical contamination of the spectrometer[24,154]. Mass spectrometers which sample the ions produced by photoionization have been incorporated into photoelectron spectrometers used to study transient species[154,155]. The mass and photoelectron spectra are not obtained in coincidence. Nevertheless, mass spectra of the reaction mixture under the same conditions as those used to take the photoelectron spectra have proved to be useful pieces of supporting data for the spectral assignment.

In the area of data treatment, subtraction techniques are frequently used to extract the complete spectrum of a transient species from a spectrum taken of the reaction mixture.

Some of the same instrumentation and experimental techniques developed to obtain photoelectron spectra of transients are being applied to related areas of research. Bock and co-workers have made extensive use of PES to analyze and optimize gas-phase reactions in flow systems[7b]. For example, the thermal decomposition of newly synthesized 1,3-dithietane and its S-oxides was analyzed by PES[156]. Several gas-phase reactions with heterogeneous catalysts have been optimized by real-time photoelectron spectroscopic analysis of the stable products[7b]. Chapter IV of this thesis describes the use of PES to detect allylic radicals as well as stable products formed in the reaction of alkenes with bismuth oxide catalyst.

The spectrometer used in the studies presented in this thesis is of standard design, modified to study the products of gas-phase pyrolysis. Chapters II and III present studies of the photoelectron spectra of organic free radicals produced by pyrolysis of organic nitrites. F. A. Houle and J. L. Beauchamp first demonstrated that alkyl and conjugated π-type radicals could be produced by pyrolysis of their appropriate nitrite precursors for observation by photoelectron spectroscopy[14,19]. Chapter IV describes the first observation by photoelectron spectroscopy of an organic radical produced by a gas-surface reaction. For these experiments the heated region contained chips of the solid over which gases could be passed. A schematic of the spectrometer is shown in Figure 1[19]. The differentially pumped source chamber, 127° electrostatic analyzer and channeltron electron multiplier are on a stainless

Figure 1. Schematic of the photoelectron spectrometer used in these experiments.


127° ELECTROSTATIC ANALYZER
CHANNELTRON HOUSING
2" DIFFUSION PUMP
PYROLYZER
SOURCE CHAMBER
HELIUM CAPILLARY DISCHARGE LAMP
4" DIFFUSION PUMP

steel baseplate in a high vacuum chamber. Magnetic fields are minimized at the analyzer by a Mumetal shield covering the analyzer and six Helmholtz coils surrounding the main vacuum chamber. The capillary discharge lamp, which can be operated with both He and Ne gases, is located below the source chamber and separated from it by differential pumping. Sample gases enter the source chamber by way of a stainless steel inlet system divided into three sections. Two sections allow calibrant gases and room-temperature samples to be introduced directly through the bottom of the source chamber. The other section connects to a flange on the side of the vacuum chamber. For the gas-surface experiments an additional inlet system that allowed independent adjustment of the pressures of two samples was connected to this flange. Gases introduced through this flange pass through a 3 mm ID quartz tube, which is used for pyrolysis, before entering the side of the source chamber. Typically, a 2 cm section of the end of the tube is wrapped with double-stranded Semflex heater wire insulated with MgO and an Inconel outer sheath. A chromel-constantan thermocouple is wedged between the wire coil and the quartz tube. Constant temperatures of up to 1000° C can be achieved. A water-cooled copper shield surrounds the heated section. The end of the quartz tube fits into a hole in the side of the source chamber. Electrons ejected normal to the plane of the photon beam and the stream of hot gases are analyzed. The spectrum is accumulated in a Tracor-Northern NS-570A multichannel scaler with 4K memory.

Only the first photoelectron band of each radical spectrum is observed in the studies presented here. This is true in general of photoelectron spectroscopic studies of organic radicals. The precursor spectrum or the spectrum of other pyrolysis or reaction products obscures the higher

bands (see Table I). However, the first band contains the most interesting chemical information since it corresponds to ionization of the unpaired electron on the radical and formation of the ground electronic state of the cation.

Carbocations have a great tendency, in the gas phase and solution, to rearrange. Since Franck-Condon factors govern the photoionization process, the photoelectron spectrum of the radical provides information about the ionic potential energy surface in the region where the geometry most closely resembles that of the radical. Thus, photoelectron spectroscopy offers a unique opportunity to study a series of well-defined carbocation isomers, those with radical-like structures. Accurate heats of formation can be derived for these species from the (apparent) adiabatic IP. The band shapes reflect changes in equilibrium geometry and force constants which occur in going from the radical to the ion.

Chapter II presents the photoelectron spectra of the C_4H_7 radicals 1-methylallyl, 2-methylallyl, allylcarbinyl and cyclobutyl radical, providing information about the corresponding $C_4H_7^+$ species in the gas phase. These cations are of long-standing interest in the cyclopropylcarbinyl, cyclobutyl and allylcarbinyl interconversions observed in solvolysis reactions. The photoelectron spectra of 1-propyl, 1-butyl, isobutyl, neopentyl and 2-butyl radicals are presented in Chapter III. The corresponding primary cations are high-energy species often postulated as intermediates or transition states in isomerization processes in both solution and in the gas phase, but not directly observed. The photoelectron spectra then yield information not available by any other experimental approach. The spectrum of 2-butyl radical completes the study of the high-energy $C_4H_9^+$ species. Combining these results with

previous studies of the 2-propyl and tert-butyl radical spectra[14], a complete picture of the $C_3H_7^+$ and $C_4H_9^+$ isomers with radical-like structures is obtained.

Interpretation of the photoelectron spectra relies on information from sources such as ESR and IR experiments performed on the radicals and theoretical and thermochemical information pertaining to both the radicals and ions. The complexities of the photoelectron spectra and the lack of more complete information about the radicals and ions preclude detailed interpretation of the spectra. Many of the conclusions must be based on trends observed among related systems. Thus, it is only with the foundation of studies of such prototypical radicals as methyl[12,13,14], ethyl[14,7a], 2-propyl[14], tert-butyl[12,14,15] and allyl radical[19] that somewhat more complex systems, as those presented in this thesis, could be studied.

At the same time, it is by comparison of the more complex with the simple systems that an increased understanding can be obtained for the sensitivity of photoelectron spectroscopy to changes in electronic structure and geometry occurring upon ionization. F. A. Houle and J. L. Beauchamp demonstrated that methyl substitution in the methyl radical, to form ethyl, 2-propyl and tert-butyl radicals, is accompanied by significant changes in the corresponding photoelectron spectra[17]. In Chapter II, analysis of the 1- and 2-methylallyl radical spectra, in comparison to the allyl radical spectrum, reveals that photoelectron spectroscopy is sensitive to the presence and position of the methyl substituent attached to the π-conjugated carbon framework. The effect of β-methyl substitution in the ethyl radical is examined in Chapter III by comparing the spectra of ethyl, 1-propyl, isobutyl and neopentyl radicals.

The changes in the photoelectron band shape can be interpreted in terms of increased C-C bond hyperconjugation with the cation center.

Equipped with a "catalogue" of organic radical photoelectron spectra, presented in Table I, the possibility of observing radicals escaping a solid surface by photoelectron spectroscopy was investigated. Chapter IV describes the results of using photoelectron spectroscopy to detect gas-phase allylic radicals, as well as stable products, formed in low-pressure gas-surface reactions between olefins and heated bismuth oxide catalyst in the presence of oxygen. The results are consistent with studies detecting only stable products or those detecting the radicals using other methods. Photoelectron spectroscopy has been shown to have potential as a general technique for monitoring both the transient and stable species directly after exiting a catalyst bed.

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CHAPTER II

Photoelectron Spectroscopy of Isomeric C_4H_7 Radicals. Implications for the Thermochemistry and Structures of the Radicals and Their Corresponding Carbonium Ions.

Photoelectron Spectroscopy of Isomeric C_4H_7 Radicals. Implications for the Thermochemistry and Structures of the Radicals and Their Corresponding Carbonium Ions.

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Abstract

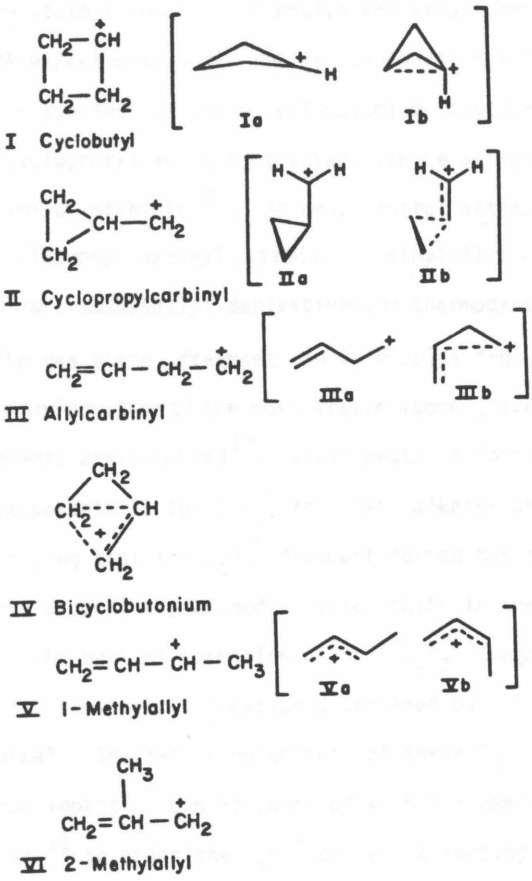
The first photoelectron bands of 1-methylallyl, 2-methylallyl, allylcarbinyl, and cyclobutyl radicals have been obtained. Adiabatic and vertical ionization potentials, respectively, are 7.49 ± 0.02 and 7.67 ± 0.02 eV for 1-methylallyl radical, 7.90 ± 0.02 and 7.95 ± 0.02 eV for 2-methylallyl radical, 8.04(+0.03,-0.1) and 8.47 ± 0.05 eV for allylcarbinyl radical and 7.54 ± 0.02 and 7.66 ± 0.02 eV for cyclobutyl radical. Using known or estimated radical heats of formation, heats of formation of the corresponding carbonium ions are calculated to be 203.1 ± 1.4 kcal/mol for 1-methylallyl cation, 212.2 ± 1.6 kcal/mol for 2-methylallyl cation, 231.0 ± 3 kcal/mol for allylcarbinyl cation and 225.1 ± 1.1 kcal/mol for cyclobutyl cation. Vibrational progressions of 990 ± 100 and 410 ± 30 cm^{-1} are resolved on the first photoelectron bands of the cyclobutyl radical and 2-methylallyl radical, respectively. Vibrational structure is observed on the 1-methylallyl radical photoelectron band, but vibrational progressions could not be assigned. The complex spectrum probably results mainly from the fact that it is ascribed to two isomers, cis- and trans-1-methylallyl radicals. The presence of vibrational structure on the first photoelectron bands of these radicals is consistent with the ions being at local minima on the $C_4H_7^+$ potential surface. Major thermal decomposition and isomerization products of 1-methylallyl, 2-methylallyl, allylcarbinyl, cyclobutyl and cyclopropylcarbinyl radicals are identified in the photoelectron spectra. No thermolysis products of 2-methylallyl radical are observed. A small amount of 1,3-butadiene and/or 2-butene is observed at high temperatures from 1-methylallyl radical. Pyrolysis of allylcarbinyl radical yields 1-methylallyl radical and 1,3-butadiene. Due

to its facile ring opening to allylcarbinyl radical (which is observed along with its thermolysis products), cyclopropylcarbinyl radical itself is not observed. Pyrolysis of cyclobutyl radical yields 1-methylallyl and 1,3-butadiene. Allylcarbinyl radical, the direct product of cyclobutyl radical ring opening is not observed, presumably because it is formed with sufficiently high internal energy to further rearrange rapidly.

Introduction

In solution, numerous experiments have been performed to gather structural, spectroscopic and kinetic data on $C_4H_7^+$ under stable ion and solvolytic conditions in order to characterize the intermediate(s) involved in the cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl interconversions[1-3]. Relatively few experiments have been performed to characterize the gas phase $C_4H_7^+$ species[4-8]. Structural identities, corresponding heats of formation and interconversion pathways of the $C_4H_7^+$ species in the gas phase are not well established.

Since photoelectron band shapes are governed by Franck-Condon factors, the photoelectron spectrum of a radical[9] provides information about the ionic potential surface in the region where the geometry most closely resembles that of the radical. In the present study, the appropriate nitrite precursors have been decomposed to yield cyclobutyl, allylcarbinyl, 1-methylallyl and 2-methylallyl radicals. These radicals have been well studied by ESR spectroscopy, yielding structural information, and their thermochemistry is known or can be estimated. The first bands in the photoelectron spectra of these C_4H_7 radicals are analyzed in this study, in conjunction with the ESR and thermochemical data for the radicals, to obtain accurate thermochemical and at least qualitative structural data for the gas phase cyclobutyl cation (I), allylcarbinyl cation (III), 1-methylallyl cation (V) and 2-methylallyl cation (VI).



The extensive experimental evidence on $C_4H_7^+$ in condensed media indicates that the solution phase species prepared from cyclobutyl or cyclopropylcarbinyl derivatives may not be represented by one static structure. Controversy continues regarding the structures involved in the equilibrium. Rapidly interconverting equivalent classical (IIa) or nonclassical (IIb) bisected cyclopropylcarbinyl cations, or equivalent bicyclobutonium cations (IV) have all been proposed. Puckered cyclobutyl cation (Ib) has been postulated as the intermediate or

transition state through which equivalent structures equilibrate. Recent NMR experiments under stable-ion conditions indicate the major, most stable species has the bicyclobutonium structure[2c,e] and the bisected cyclopropylcarbinyl structure can be assigned to a minor species of very similar stability[2c]. An unsuccessful attempt has been made to determine whether cyclopropylcarbinyl cation or 1-methylallyl cation (V), which can be prepared from 1-methylallyl derivatives, is thermodynamically more stable in solution[3].

In the gas phase, fragment ion thresholds from hydrocarbons often correspond to formation of the most stable isomer, even when extensive rearrangements are required[10]. Ionic heats of formation corresponding to appearance potentials for $C_4H_7^+$ from many alkanes and alkenes are very close, implying that the $C_4H_7^+$ fragment formed has a common structure[4]. Taking into account a presumed kinetic shift in the appearance potential, the heat of formation of this $C_4H_7^+$ fragment ion coincides with that of 1-methylallyl cation determined by ionization of 1-methylallyl radical. Ionization potentials of three C_4H_7 radicals, determined by electron impact[4,5] can be combined with the heats of formation of the radicals[11] to order the $C_4H_7^+$ cations according to increasing heats of formation: 1-methylallyl, 2-methylallyl and cyclobutyl cation.

Some experiments have been done in the gas phase to determine the stable $C_4H_7^+$ species and to study the interconversion of isomers. Measurements of the kinetic energy released when five isomers of $(C_4H_7Br)^+$ lose Br to form $C_4H_7^+$ indicate that cyclopropylcarbinyl and allylcarbinyl cations can rearrange with little activation energy to a more stable species; however, cyclobutyl cation and 1- and 2-methylallyl cations exist in potential wells in the gas phase[6]. In elegant

radiochemical experiments, β-decay by cyclobutane $C_4H_{7-n}T_{n+1}$ yields $C_4H_{7-n}T_n^+$ cations which react with a nucleophile to yield cyclobutyl and cyclopropylcarbinyl products, indicating that gas phase cyclobutyl cations exist for at least 10^{-9} sec in a cyclic structure[7]. A different multi-step trapping technique has been used to identify the $C_4H_7^+$ ions formed by fragmentation of protonated cyclopropylcarbinol and bromocyclobutane[8]. After neutralization of the ions by electron capture, the ensuing radicals are trapped in a fast reaction with a neutral. The products of this reaction, after ionization by electron capture, are analyzed using mass selected collisional mass spectroscopy. The results of these experiments indicate that an identical mixture of $C_4H_7^+$ ions was formed during the time before their neutralization (~10^{-5} - 10^{-4} sec), regardless of whether the initial ions had the cyclobutyl or cyclopropylcarbinyl structure. This mixture consisted of 36 ± 10% cyclobutyl, 47 ± 10% allylcarbinyl or cyclopropylcarbinyl and 17 ± 10% tertiary methylcyclopropyl or secondary allyl ions.

Various theoretical approaches have been used to predict the relative stabilities of the $C_4H_7^+$ cation intermediates[12,13]. Recent ST04-31G ab initio molecular orbital calculations have determined that bisected cyclopropylcarbinyl cation (IIa) and a structure coinciding approximately to formulations for bicyclobutonium ion (IV) are at local minima on the $C_4H_7^+$ potential surface; puckered cyclobutyl cation (Ib) collapses without barrier to bisected cyclopropylcarbinyl cation[13c]. At the STO-3G level, allylcarbinyl cation (IIIa and b) also collapses without barrier to bisected cyclopropylcarbinyl cation[13b]. No local minimum corresponding to cyclobutyl cation with a less puckered ring and a more planar cation center (Ia) was found, this species being higher in energy

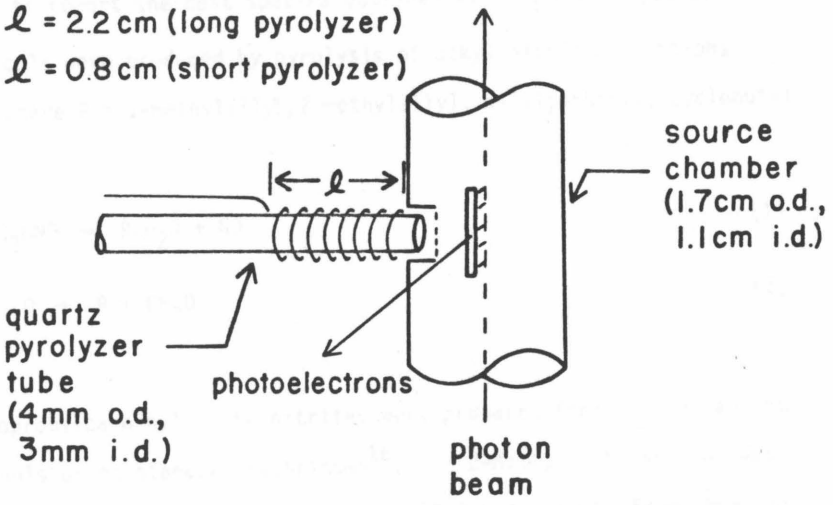
than puckered cyclobutyl cation[13d].

As yet there is no consistent picture of the $C_4H_7^+$ system in the gas phase. For example, theory has failed to find a local minimum corresponding to cyclobutyl cation, but experiments seem to indicate it is a stable gas phase species. A bicyclobutonium ion has been found by theory to be at a local minimum, but without gas phase spectroscopic information on the ions, the results of trapping experiments are interpreted only in terms of classical ion structures. Condensed phase results cannot automatically be applied to the gas phase. The effects on structures and energies of carbonium ions in going from the gas phase into stable-ion media have been studied[14]. Differences in solvation among carbonium ion isomers and rearrangement transition states appear to be small. However, some evidence indicates that the largest differences occur when there are significant changes in the extent of charge delocalization in the cation. Thus, the $C_4H_7^+$ system should provide an interesting test of differential solvation effects. In the present study we report C_4H_7 radical photoelectron spectra which provide structural and thermochemical information about several gas phase $C_4H_7^+$ isomers. Our analysis of the data indicates these isomers have structures corresponding most closely to slightly puckered cyclobutyl cation (Ia), primary allylcarbinyl cation (IIIa), 1-methylallyl cation (Va and b) and 2-methyallyl cation (VI). In addition, thermal decomposition and isomerization products of 1- and 2-methylallyl, allylcarbinyl, cyclobutyl and cyclopropylcarbinyl radicals are identified in the photoelectron spectra. Cyclopropylcarbinyl radical itself is not observed, due to its facile ring-opening isomerization to allylcarbinyl radical.

Experimental

Photoelectron spectra were recorded on a spectrometer of standard design, which has been modified to study the products of gas phase pyrolysis. A detailed description has been given elsewhere[15]. A schematic of the pyrolysis and photoionization regions is shown in Figure 1. Pyrolysis takes place in a quartz tube, the end of which is wrapped with double-stranded, insulated heating wire. A thermocouple (not shown in Figure 1) is wedged between the wire and the quartz tube to monitor the temperature. The tip of the tube is inserted into an aperture in the source chamber. The photon beam is directed along the axis of the cyclindrical source chamber. Photoelectrons ejected perpendicular to the quartz tube and the photon beam are energy analyzed. Most of the experiments were done using a long pyrolyzer (ℓ = 2.2 cm) at temperatures from 500 to 700° C. Since the pyrolysis is done at low pressures (~10^{-2} torr), molecules are heated mainly by collisions with the wall of the pyrolyzer, and there are fewer molecule-molecule collisions. During the ~1 msec residence time of a molecule in the long pyrolyzer, it experiences ~150 collisions with the wall, and ~50 collisions with other molecules. Unimolecular radical processes result primarily from activation on the pyrolyzer wall and may, in fact, occur while the molecule is in contact with the surface. In an attempt to increase the concentration of the initial radical formed by decreasing the radical pyrolysis products, a short pyrolyzer (ℓ = 0.8 cm) was used for some experiments. Pyrolysis temperatures from ~80-130° C higher were necessary with the shorter pyrolyzer to obtain the same amount of precursor decomposition achieved with the long pyrolyzer. Spectra

Figure 1: Schematic of the pyrolyzer and photoionization region.


ℓ = 2.2 cm (long pyrolyzer)
ℓ = 0.8 cm (short pyrolyzer)
ℓ
source chamber (1.7cm o.d., 1.1cm i.d.)
quartz pyrolyzer tube (4mm o.d., 3mm i.d.)
photoelectrons
photon beam

showing the same amount of precursor decomposition were compared and no increase of the primary radical products nor decrease in the secondary radical products, compared to the amount of nitrite decomposition, was apparent. Furthermore, there is no evidence that the slightly higher pyrolysis temperatures change the shapes of the radical spectra (due to a temperature-dependent population of radical conformations or higher vibrational states) and in particular no hot bands were observed. We choose to report the best spectra obtained with both pyrolyzers.

Radicals were produced by pyrolysis of alkyl nitrites, reactions 1 and 2, where R = 1-methylallyl, 2-methylallyl, allylcarbinyl, cyclobutyl

$$RCH_2ONO \rightarrow RCH_2O + NO \qquad (1)$$

$$RCH_2O \rightarrow R + CH_2O \qquad (2)$$

and cyclopropylcarbinyl. The nitrites were prepared from the corresponding alcohols using standard techniques[16]. 2-Methyl-3-buten-1-ol was obtained from Chemical Samples Co., 3-methyl-3-buten-1-ol from Chemical Dynamics Corp., and cyclobutanemethanol and 4-penten-1-ol from Aldrich. 2-Cyclopropanethanol was prepared from cyclopropyl bromide (Aldrich). Cyclopropyl bromide was reacted with finely divided lithium in diethyl ether, giving a solution of cyclopropyllithium[17]. 2-Cyclopropanethanol was then obtained by reacting this solution with ethylene oxide[18]. The alcohol was purified by gas phase chromotography. To produce separately the cis and trans isomers of 1-methylallyl radical as the initial pyrolysis products, cis and trans-3-penten-1-ol were used to

make the nitrite precursor. To prepare cis-3-penten-1-ol, pent-3-yn-1-ol (Farchan) was hydrogenated at room temperature and atmospheric pressure in the presence of a palladium-calcium carbonate catalyst and using ethyl acetate as solvent[19]. To prepare trans-3-penten-1-ol, pent-3-yn-1-ol was reacted with sodium in liquid ammonia under argon atmosphere and the reaction was quenched with ammonium chloride[20]. Purified products were analyzed by capillary gas chromatography (SE-30 column at 60 °C). The cis-3-penten-1-ol was >95% pure, the major impurity being pent-3-yn-1-ol. The trans-3-penten-1-ol was 99% pure. The nitrites prepared from these alcohols were also analyzed and found to be 90% pure, the major impurity being the alcohols with <2% of the other nitrite isomer.

Alkyl nitrites have an activation energy of ~40 kcal/mol toward decomposition to NO and alkoxy radicals (reaction (1))[21]. Alkoxy radicals are quite unstable thermally. For example, the activation energy for decomposition of C_2H_5O to CH_3 and CH_2O is 21.6 kcal/mol[21]. The intermediate alkoxy radicals have never been observed in these experiments, but since their ionization potentials are expected to be ~9.2 eV [22], their spectra would be at least partially obscured by precursor and product photoelectron spectra.

The activation energy for alkyl nitrite decomposition is comparable to activation energies for decomposition or isomerization of the initial alkyl radicals produced by nitrite decomposition. Thus, in one spectrum, undecomposed nitrite, the initial alkyl radical and products from unimolecular and possibly wall reactions of this radical can be identified. By changing the pyrolysis temperature, the extent of radical decomposition present in the spectrum can be varied.

When necessary, spectra were recorded using both He I and Ne I radiation in order to determine those spectral features arising from He Iβ ionization. Energy scales were calibrated using the peaks due to CH_2O, NO, Ar and 1,3-butadiene. CH_2O and NO result from the nitrite decomposition. The first two peaks of the butadiene photoelectron spectrum nearly coincide with the He Iβ line of CH_2O and the first NO peak. They were used for calibration purposes when butadiene appeared as a major decomposition product and its spectrum was the dominant feature in the 9.0-9.5 eV spectral region. Spectra of authentic samples of 1-butene, cis- and trans-2-butene, and 1,3-butadiene were recorded in our laboratory and used along with published adiabatic ionization potentials of these molecules [23,24] for comparison with nitrite pyrolysis spectra. Resolution for these experiments was approximately 30-40 mV. Reported ionization potentials are the average of several determinations. Error limits indicate the reproducibility of the numbers, except for the ionization potentials of allylcarbinyl radical where circumstances described below required larger error limits.

Results

Spectra obtained in these experiments are presented in Figures 2-8. The C_4H_7 radical photoelectron data are summarized in Table I. Spectra of the initial alkyl radical products and the results of their decomposition or isomerization were identified by considering the temperature-dependent nitrite thermolysis spectra together with thermal decomposition mechanisms for C_4H_7 radicals reported in the literature, and published spectra or spectra taken in our laboratory of possible decomposition products.

Table I. C_4H_7 Radical Photoelectron Data

Radical	Ionization Potential (eV) Adiabatic	Vertical	Vibrational Structure (cm^{-1})
1-Methylallyl	7.49 ± 0.02	7.67 ± 0.02	Observed
2-Methylallyl	7.90 ± 0.02	7.95 ± 0.02	410 ± 30
Allylcarbinyl	8.04(+0.03-0.1)	8.47 ± 0.05	None observed
Cyclobutyl	7.54 ± 0.02	7.66 ± 0.02	990 ± 100

Nitrites. The photoelectron spectra of 2-methyl-3-buten-1-yl nitrite, 3-methyl-3-buten-1-yl nitrite, 4-penten-1-yl nitrite, cyclobutanemethyl nitrite and 2-cyclopropanethyl nitrite are presented in Figure 2. The vertical ionization potentials (IPs) of these species are approximately 10.0, 9.5, 9.9, 10.2 and 10.6 eV, respectively.

1-Methylallyl Radical. A spectrum of the pyrolysis products of the 2-methyl-3-buten-1-yl nitrite precursor to 1-methylallyl radical, recorded with He I radiation and using the short pyrolyzer at 740 °C is shown in Figure 3. This precursor would be expected to yield some mixture of cis and trans-1-methylallyl radicals. Maximum count rates on the 1-methylallyl radical band were ~70 sec^{-1}. Vibrational fine structure is resolved on this band, and the prominent features are indicated in the figure inset. However, vibrational progressions could not be assigned. The adiabatic IP was chosen as the first peak of the vibrational fine structure, at 7.49 ± 0.02 eV, and the vertical IP as the most intense feature, at 7.67 ± 0.02 eV. The observed adiabatic and vertical IPs would be expected to depend on the isomeric composition of the 1-methylallyl radical population. A previous determination by electron impact yielded an ionization potential of 7.54 ± 0.05 eV for 1-methylallyl radical[4].

In an attempt to obtain separate photoelectron spectra of the cis and trans isomers of 1-methylallyl radical, precursors which produce only one of the isomers as their initial pyrolysis product were pyrolyzed at a low temperature (490 °C using the long pyrolyzer). No difference between the 1-methylallyl radical spectrum from the cis, trans and non-specific isomer precursors, cis-3-penten-1-yl nitrite, trans-3-penten-1-yl nitrite and 2-methyl-3-buten-1-yl nitrite, respectively, could be

Figure 2: He I spectra of (a) 2-methyl-3-buten-1-yl nitrite, (b) 3-methyl-3-buten-1-yl nitrite, (c) penten-1-yl nitrite, (d) cyclobutanemethyl nitrite and (e) 2-cyclopropanethyl nitrite.

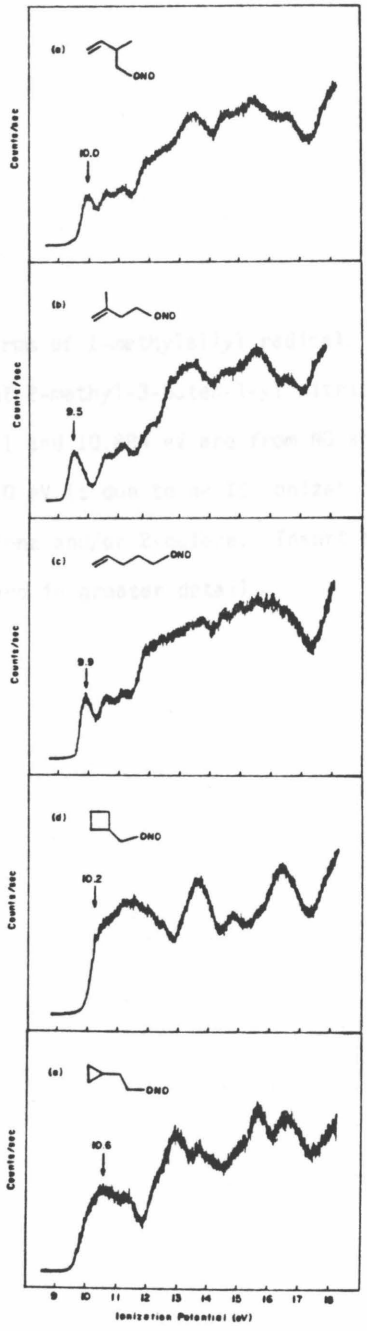
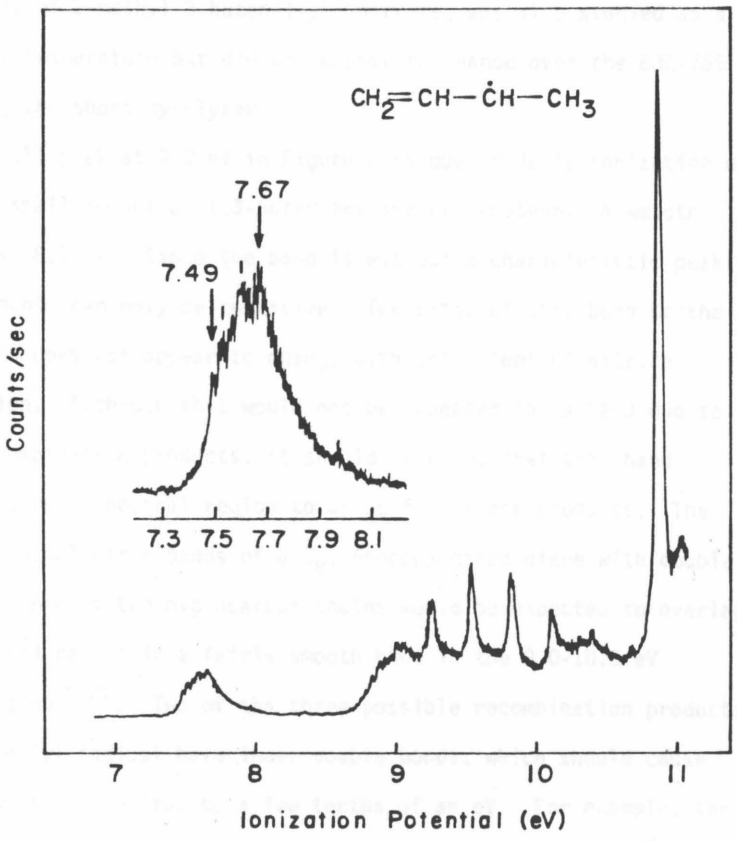

(a)
ONO
10.0
Counts/sec
(b)
ONO
9.5
Counts/sec
(c)
ONO
9.9
Counts/sec
(d)
ONO
10.2
Counts/sec
(e)
ONO
10.6
Counts/sec
9 10 11 12 13 14 15 16 17 18
Ionization Potential (eV)

Figure 3: He I spectrum of 1-methylallyl radical. Other pyrolysis products of 2-methyl-3-buten-1-yl nitrite are observed. Peaks at 9.2-10.1 and 10.884 eV are from NO and CH_2O, respectively. Peak at 9.0 eV is due to He Iβ ionization of CH_2O and some 1,3-butadiene and/or 2-butene. Insert shows 1-methylallyl radical band in greater detail.


CH2=CH—ĊH—CH3
7.67
7.49
7.3 7.5 7.7 7.9 8.1
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

discerned. This indicates that either the photoelectron spectra of the cis and trans radicals are very similar or that the radical isomers interconvert even at a low pyrolysis temperature under our experimental conditions. The 1-methylallyl radical photoelectron spectrum, obtained by pyrolysis of 2-methyl-3-buten-1-yl nitrite, was also studied as a function of temperature but did not appear to change over the 630-765 °C range using the short pyrolyzer.

The small peak at 9.0 eV in Figure 3 is due to He Iβ ionization of CH_2O and a small amount of 1,3-butadiene and/or 2-butene. A smooth band begins ~8.7 eV. Since the band is without a characteristic peak, any assignment can only be tentative. The ratio of this band to the radical band does not appear to change with the extent of nitrite decomposition. Although this would not be expected for a band due to radical recombination products, it should be noted that this band is in the correct spectral region to arise from these products. The first two photoelectron bands of a C_8, nonconjugated diene with double bonds at the end of the hydrocarbon chains would be expected to overlap each other and result in a fairly smooth band in the 9.0-10.5 eV spectral region[25,26]. Two of the three possible recombination products of 1-methylallyl radical have inner double bonds, which should cause the spectrum to be shifted by a few tenths of an eV. For example, the adiabatic IP of 2-butene is 0.5 eV lower than that of 1-butene[23]. Similar smooth bands in the allyl[15] and 2-methylallyl radical spectra, located in the 9-10 eV spectral region could also be due to dienes produced by radical recombination.

Photoionization of a radical in its doublet state can produce both singlet and triplet spin states of the ion. No calculations of the

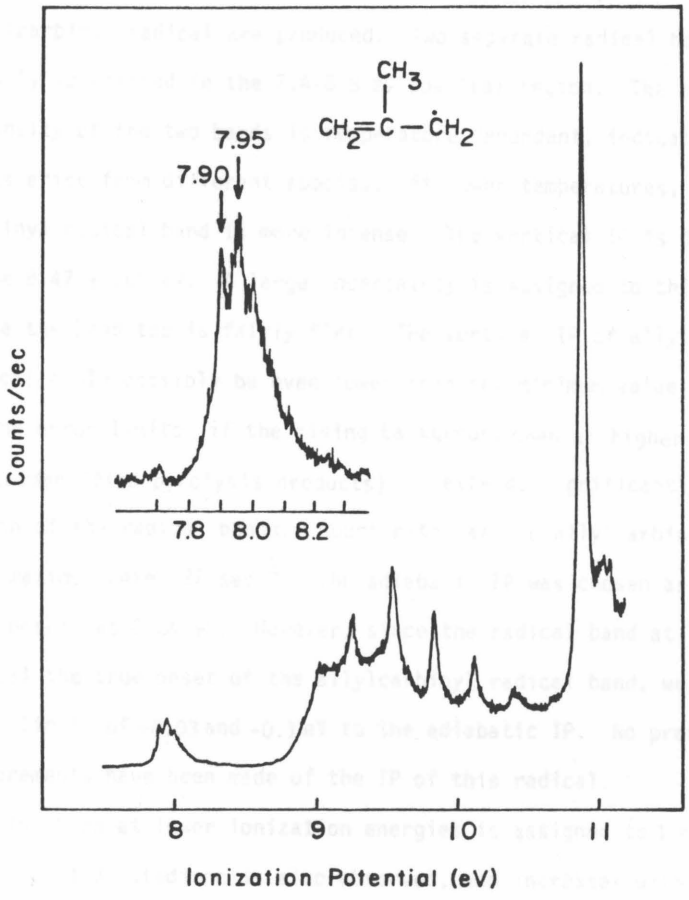
excited triplet state of 1-methylallyl cation have been done. However, the energy gap between the ground and first excited triplet state of 1-methylallyl cation would not be expected to differ greatly from that for allyl cation. The first excited triplet state of allyl cation has been calculated to be 3.01[27] and 3.67 eV[28] above the ground state. Therefore, it is unlikely that the first excited triplet state of the 1-methylallyl cation gives rise to the band observed at ~9 eV. A discrete band in the 10-11 eV spectral region could not be identified.

2-Methylallyl Radical. The photoelectron spectrum of the pyrolysis products of the 2-methylallyl radical precursor, using the short pyrolyzer at 739 °C, is shown in Figure 4. Count rates at the radical band maximum were ~115 sec^{-1}. Vibrational fine structure is clearly resolved. The first two peaks of the vibrational progession, at 7.90 ± 0.02 and 7.95 ± 0.02 eV, correspond to the adiabatic and vertical IPs respectively. A third peak is also resolved. The spacing between the peaks is more highly reproducible than their positions and was determined to be 0.051 ± 0.003 3V (410 ± 30 cm^{-1}). A previous electron impact determination yielded an IP of 7.89 eV[4], in excellent agreement with our adiabatic IP.

The band with an onset ~8.8 eV may be due to the 2-methylallyl radical recombination product, as discussed above. No discrete band ~3 eV above the first photoelectron band of 2-methylallyl radical, which might be assigned to the first excited triplet state of the cation, could be identified.

Allylcarbinyl Radical. An isolated spectrum of allylcarbinyl radical could not be obtained. At temperatures necessary for nitrite pyrolysis,

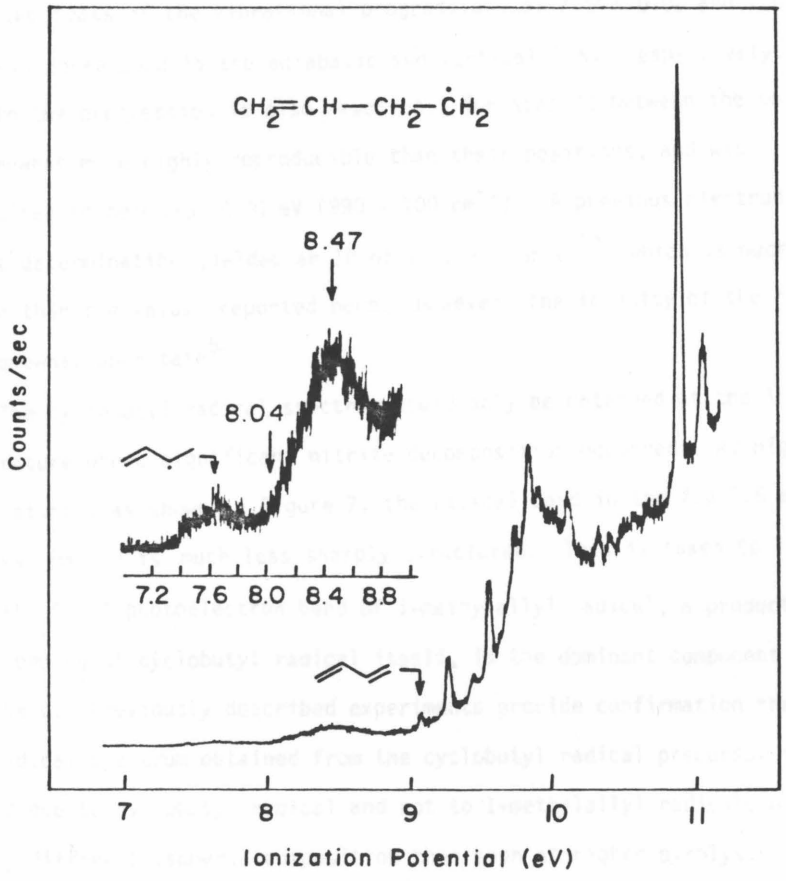
Figure 4: He I spectrum of 2-methylallyl radical. Other observed pyrolysis products of 2-methylallyl radical nitrite precursor are NO and CH_2O. Insert shows 2-methylallyl radical band in greater detail.


CH3
CH2=C—ĊH2
7.95
7.90
7.8
8.0
8.2
Counts/sec
8
9
10
11
Ionization Potential (eV)

allylcarbinyl radical itself isomerized or decomposed to products, the spectra of which overlapped its own. Figure 5 is a Ne I spectrum of the pyrolysis products of the allylcarbinyl radical precursor taken using the short pyrolyzer at the lowest temperature (583 °C) where significant amounts of the allylcarbinyl radical are produced. Two separate radical bands can be clearly identified in the 7.4-8.8 eV spectral region. The relative intensity of the two bands is temperature dependent, indicating the bands arise from different species. At lower temperatures, the allylcarbinyl radical band is more intense. The vertical IP is determined to be 8.47 ± .05 eV. A large uncertainty is assigned to this value since the band top is fairly flat. The vertical IP of allylcarbinyl radical could possibly be even lower than the minimum value included in the error limits if the rising background seen at higher IPs (due to unidentified pyrolysis products) extends significantly into the region of the radical bands. Count rates at the allylcarbinyl radical band maximum were ~22 sec^{-1}. The adiabatic IP was chosen as the apparent band onset, at 8.04 eV. However, since the radical band at lower IP may conceal the true onset of the allylcarbinyl radical band, we assign error limits of +0.03 and -0.1 eV to the adiabatic IP. No previous measurements have been made of the IP of this radical.

The band at lower ionization energies is assigned to 1-methylallyl radical. 1,3-Butadiene is also observed, and increases with pyrolysis temperature. The peaks at 9.7 and 9.9 eV, which are small in the low temperature spectrum, increase with temperature. A small peak at 10.3 eV is only observed at low temperatures. These features are not due to any expected decomposition product of C_4H_7 radicals, and perhaps indicate alternative decomposition pathways for the nitrite precursor.

Figure 5: Ne I spectrum of allylcarbinyl radical. 1-Methylallyl radical (7.4-8.0 eV), 1,3-butadiene, NO and CH_2O are also observed as pyrolysis products of allylcarbinyl radical nitrite precursor. Insert shows allylcarbinyl radical band in greater detail.


CH2=CH—CH2—ĊH2
8.47
8.04
7.2 7.6 8.0 8.4 8.8
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

Cyclobutyl Radical. Shown in Figure 6 is a spectrum taken with He I radiation of the pyrolysis products of the cyclobutyl radical precursor produced using a low pyrolysis temperature (595 °C) for the short pyrolyzer. Count rates at the cyclobutyl radical band maximum were ~45 sec^{-1}. Vibrational fine structure appears on the cyclobutyl radical band. The first two peaks of the vibrational progression, at 7.54 ± 0.02 and 7.66 ± 0.02 eV, correspond to the adiabatic and vertical IPs, respectively. A third peak in the progression is also resolved. The spacing between the peaks is somewhat more highly reproducible than their positions, and was determined to be 0.123 ± 0.01 eV (990 ± 100 cm^{-1}). A previous electron impact determination yielded an IP of 7.88 ± 0.05 eV[5a], which is much higher than the values reported here. However, the identity of the radical was somewhat uncertain[5b].

The cyclobutyl radical spectrum could only be obtained at the lowest temperature where significant nitrite decomposition occurred. At higher temperatures, as shown in Figure 7, the radical band in the 7.3-7.8 eV spectral region is much less sharply structured. This is taken to indicate that the first photoelectron band of 1-methylallyl radical, a product of ring opening of cyclobutyl radical itself, is the dominant component of this band. Previously described experiments provide confirmation that the radical spectrum obtained from the cyclobutyl radical precursor is indeed due to cyclobutyl radical and not to 1-methylallyl radicals of a very different isomeric composition than seen at higher pyrolysis temperatures. Under the same conditions at which the cyclobutyl radical band is observed, pyrolysis of the precursors which specifically form either cis or trans-1-methylallyl radical as their initial product results in the same rounded, weakly structured 1-methylallyl radical band.

Figure 6: He I spectrum of cyclobutyl radical. NO, CH_2O and 1,3-butadiene are also observed as pyrolysis products of cyclobutyl radical nitrite precursor. Insert shows cyclobutyl radical band in greater detail.

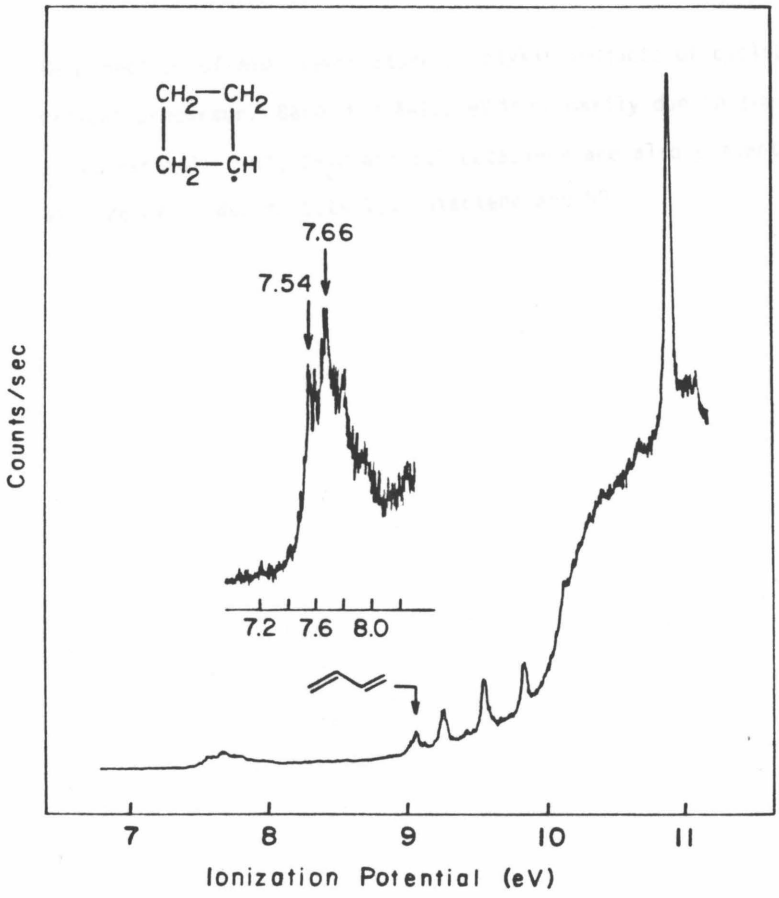
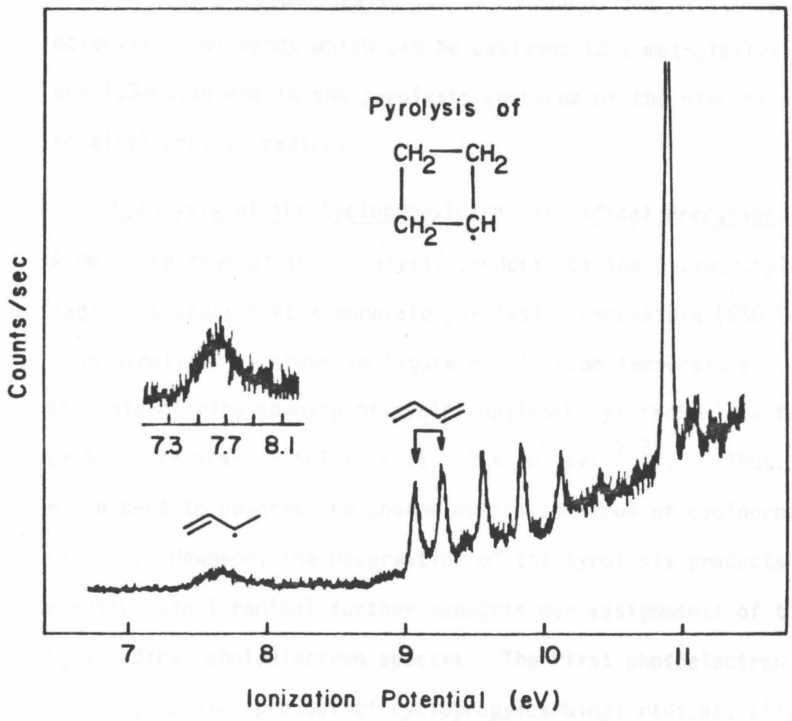

CH2—CH2
CH2—ĊH
7.66
7.54
7.2 7.6 8.0
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

Figure 7: He I spectrum of high-temperature pyrolysis products of cyclobutyl radical precursor. Band at 7.4-7.9 eV is primarily due to 1-methyl-allyl radical. NO, CH_2O and 1,3-butadiene are also present. Peak at 9.26 eV is due to both 1,3-butadiene and NO.


Pyrolysis of
CH2—CH2
CH2—ĊH
7.3
7.7
8.1
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

1,3-Butadiene, present at low temperatures, increases with temperature.

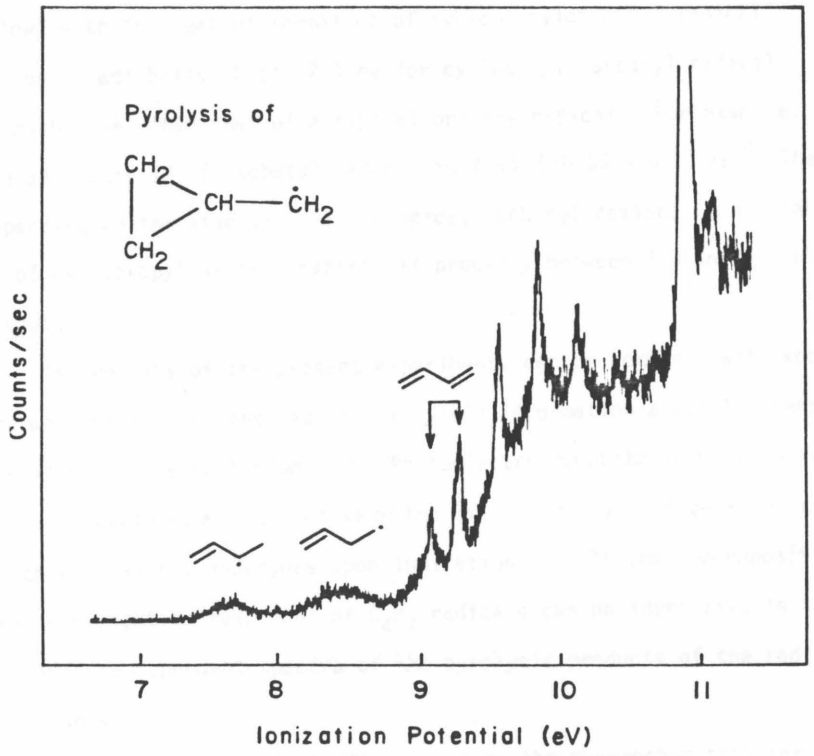
As discussed in the section on radical thermal decomposition and isomerization, the direct product of cyclobutyl radical ring opening is presumably the allylcarbinyl radical, but since it is born with ~35 kcal/mol internal energy it quickly isomerizes to 1-methylallyl radical and/or decomposes to 1,3-butadiene. This is supported by the observation of bands which can be assigned to 1-methylallyl radical and 1,3-butadiene in the pyrolysis spectrum of the nitrite precursor to allylcarbinyl radical.

Pyrolysis of the Cyclopropylcarbinyl Radical Precursor.

A He I spectrum of the pyrolysis products of the cyclopropylcarbinyl radical precursor at a moderate pyrolysis temperature (550 °C) for the long pyrolyzer is shown in Figure 8. At room temperature the rate of ring opening of cyclopropylcarbinyl radical to form allylcarbinyl radical in solution is 1.3×10^{8} sec^{-1} [29]. Thus, we would not expect to observe the photoelectron spectrum of cyclopropylcarbinyl radical. However, the observation of the pyrolysis products of cyclopropylcarbinyl radical further supports our assignments of the other C_4H_7 radical photoelectron spectra. The first photoelectron bands of the ring-opened product of cyclopropylcarbinyl radical, allylcarbinyl radical, and the isomerization product of allylcarbinyl radical, 1-methylallyl radical, are observed. The relative intensity of the bands is temperature dependent, the allylcarbinyl radical spectrum being more intense at lower temperatures. 1,3-Butadiene is also observed.

No unassigned alkyl radical band was observed in the pyrolysis spectra of the cyclopropylcarbinyl radical precursor, although a weak

Figure 8: He I spectrum of pyrolysis products of cyclopropylcarbinyl radical nitrite precursor. 1-Methylallyl radical, allylcarbinyl radical, 1,3-butadiene, NO and CH_2O are present. Peak at 9.26 eV is due to both 1,3-butadiene and NO.


Pyrolysis of
CH2
CH
CH2
CH2
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

band due to cyclopropylcarbinyl radical in the 7.5-9.0 eV spectral region would be obscured by the photoelectron bands of products of cyclopropylcarbinyl radical rearrangement. It is difficult to estimate the IP of cyclopropylcarbinyl radical. Combining one tentative heat of formation for cyclopropylcarbinyl cation of 212 kcal/mol [30-32] (see discussion below) with the heat of formation of cyclopropylcarbinyl radical [33] yields an adiabatic IP of ~7.1 eV for cyclopropylcarbinyl radical. This is much lower than that of a typical primary radical. For example, the adiabatic IP of isobutyl radical is 7.93 (+0.03 - 0.1) eV[34]. Therefore, depending on the stability of cyclopropylcarbinyl cation, the adiabatic IP of cyclopropylcarbinyl radical is probably between 7.0 and 8.0 eV.

Discussion

The results of the present experiments can be combined with known thermochemistry for the radicals to yield information about the thermochemistry of the carbonium ions. Photoelectron band shapes and resolved vibrational structures are indicative of the extent and type of geometry changes which the radical undergoes upon ionization. Thermal decomposition and isomerization reactions of C_4H_7 radicals can be identified in the temperature-dependent spectra of the pyrolysis products of the radical precursors.

Thermochemistry. Table II summarizes the thermochemistry for the 1-methylallyl, 2-methylallyl, allylcarbinyl and cyclobutyl systems. From known radical heats of formation and the adiabatic IPs determined from the photoelectron spectra, the heats of formation of the corresponding ions in their ground electronic states with structures similar to those of the radicals can be determined. These cation heats of formation are

Table II. Thermochemical Data for 1-Methylallyl, 2-Methylallyl, Allylcarbinyl and Cyclobutyl Systems[a]

R	$\Delta H_f(R)$[b]	$\Delta H_f(R^+)$[c,d]	D(R-H)[c,e]	$D(R^+-H^-)$[c.e]	PA(olefin)[e]
1-Methylallyl	30.4	203.1	82.7[g]	238.0[g]	188.7
2-Methylallyl	30.0	212.2	86.4	251.2	---
Allylcarbinyl	45.6[f]	231.0	97.9[f]	265.9	160.8
Cyclobutyl	51.2	225.1	96.5	253.0	178.1

a. All values in kcal/mol at 298 K.

b. Taken from Ref. 11, except for allylcarbinyl radical.

c. Ionic heats of formation are calculated using the convention that the heat of formation of an electron at rest is zero at all temperatures. Accordingly, $\Delta H_f(H^+)$ = 365.7 kcal/mol and $\Delta H_f(H^-)$ = 34.7 kcal/mol (Ref. 37).

d. Error limits ± 1.4 kcal/mol for 1-methylallyl; ± 1.6 kcal/mol for 2-methylallyl; ±3 kcal/mol for allylcarbinyl; ±1.1 kcal/mol for cyclobutyl.

e. Alkane and olefin heats of formation from Ref. 38.

f. ΔH_f(allylcarbinyl) calculated assuming D(R-H) = D(n-propyl-H) taken from Ref. 11.

g. Olefin is 1-butene. D(R-H) = 85.5 kcal/mol and $D(R^+-H^-)$ = 240.8 kcal/mol if trans-2-butene is the olefin.

necessarily subject to change with the radical heats of formation[35]. The relative energetics of the radicals and ions are shown in Figure 9. Not all of these ionic species may be at local minima on the $C_4H_7^+$ potential energy surface. In particular, allylcarbinyl cation may not be at a local minimum[6,13b]. Although experimental evidence seems to indicate that cyclobutyl cation is a stable gas-phase species[6-8], theory has not found a local minimum corresponding to this structure[13a,c]. If the cation with the radical-like structure is not at a local minimum, then the apparent adiabatic IP reported here for the radical is not a true adiabatic IP since the ion is not formed in a ground vibrational state. However, because Franck-Condon factors govern the photoionization process, the apparent adiabatic IP still is a very useful thermochemical quantity. It corresponds to formation of the most stable cation obtained by small deviations from the radical geometry. By combining the heat of formation for the ion with alkane and alkene heats of formation, the hydride affinity of the ion and the proton affinity of the corresponding alkene can be determined. Since typical primary, secondary and tertiary ions have characteristic hydride affinities[39,40], the hydride affinities of the $C_4H_7^+$ ions can be used to evaluate their relative stabilities. In Figure 10, hydride affinities[41] derived from the photoelectron data on the corresponding radicals presented in the work of Beauchamp and coworkers[15,34,42-44] are shown for comparison with the $C_4H_7^+$ hydride affinities.

The heat of formation of 1-methylallyl cation is 203.1 ± 1.4 kcal/mol. This is consistent with a heat of formation of 199 kcal/mol calculated from the measured proton affinity of 1,3-butadiene[30,31]. The

Figure 9: Heats of formation of C_4H_7 radicals and ions and C_4H_7 radical rearrangement energetics.

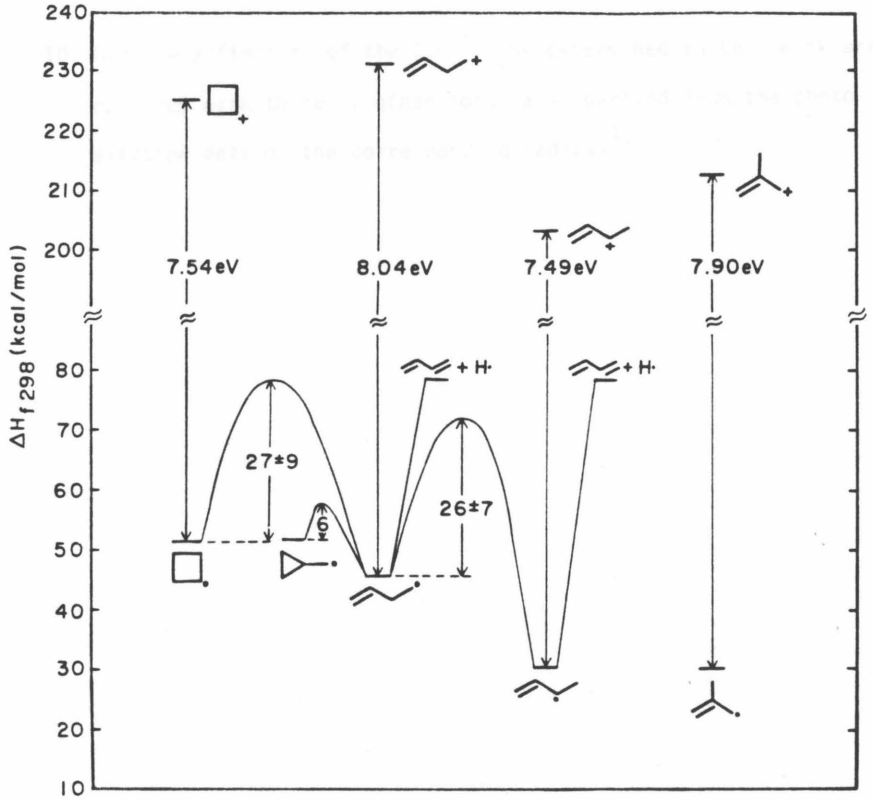
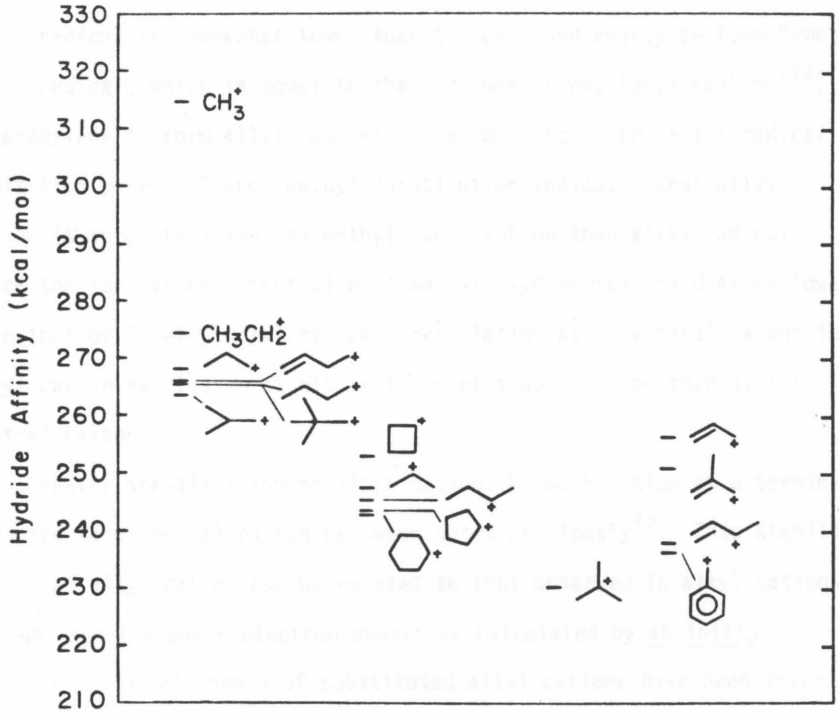

240
230
220
210
200
80
70
60
50
40
30
20
10
ΔH f 298 (kcal/mol)
7.54eV
8.04eV
7.49eV
7.90eV
27±9
6±1
26±7
+ H·
+ H·

Figure 10: Hydride affinities of the $C_4H_7^+$ ions determined in this work are compared with those of other ions also derived from the photoelectron data of the corresponding radical[41].


Hydride Affinity (kcal/mol)
330
320
310
300
290
280
270
260
250
240
230
220
210
– CH3+
– CH3CH2+

heat of formation of 2-methylallyl cation is 212.2 ± 1.6 kcal/mol. The adiabatic IPs of 1-methylallyl and 2-methylallyl radicals are 0.64 and 0.23 eV lower, respectively, than that of the parent allyl radical[15]. Methyl substitution at the terminal carbon has a small stabilizing effect and at the central carbon has no apparent effect on the allylic radical, as indicated by the homolytic bond energies of the corresponding olefins. The C-H bond energies in the butenes, listed in Table II, to form 1-methylallyl radical are somewhat lower than the C-H bond energy to form 2-methylallyl radical, which is equal to the C-H bond energy (86.3 kcal/mol[11]) in propylene to form allyl radical. The lowering of the allyl radical ionization potential upon methyl substitution indicates that allyl cation is more stabilized by methyl substitution than allyl radical. Since the ionization potential of 1-methylallyl radical is 0.41 eV lower than that of 2-methylallyl radical, methylation at a terminal carbon in allyl cation results in significantly more stabilization than at the central carbon.

Greater stabilization of allyl cations by methylation at a terminal compared to a central carbon has been noted previously[45]. This stabilization of allyl cation can be related to that observed in alkyl cations. ^{13}C NMR spectra and π-electron densities calculated by *ab initio* molecular orbital theory of substituted allyl cations have been interpreted by considering two contributing ionic resonance structures, the ionic center being on either of the two terminal allylic carbons[45,46]. Both resonance structures for 2-methylallyl cation have primary ionic centers, like allyl cation. In this case, the amount of stabilization is what would be expected for methyl substitution at a carbon one

removed from a primary alkyl cation center. The hydride affinity of 2-methylallyl cation (251.6 kcal/mol) is 4.8 ± 2 kcal/mol less than that of allyl cation (256.4 kcal/mol [15,41]). This is equal to the 5.0 ± 3 kcal/mol stabilization observed when the hydride affinity of isobutyl cation (263.4 kcal/mol) is compared to that of n-propyl cation (268.4 kcal/mol)[34,41]. β-Methyl stabilization of primary alkyl cations has been ascribed to both inductive and hyperconjugative effects[47]. In the case of 1-methylallyl cation, one resonance structure has a secondary and the other a primary cationic center. Referring to Figure 10, the hydride affinity of 1-methylallyl cation (238.0 or 240.8 kcal/mol, to form 1- or 2-butene, respectively) is consistent with that which would have been predicted (~244 kcal/mol) for an allylic resonance stabilized average of a primary and secondary C_4 cation.

The heat of formation and hydride affinity of allylcarbinyl cation are 231.0 and 265.9 ± 3 kcal/mol, respectively. The adiabatic IP of allylcarbinyl radical is 8.04(+0.03,-0.1)eV. This is comparable to adiabatic IPs of other primary radicals, such as n-propyl (8.15 ± 0.02 eV)[34] and n-butyl (8.02 + 0.04 - 0.1)[34]. The hydride affinity of allylcarbinyl cation is also comparable to hydride affinities of other primary cations, as seen in Figure 10. Thus, allylcarbinyl cation appears to be a typical primary cation represented by structure IIIa, not stabilized by charge delocalization, as shown in structure IIIb. However, the hydride affinity is not known better than ±3 kcal/mol. If stabilization due to charge delocalization were less than or equal to ~3 kcal/mol, it cannot be detected in these experiments.

The heat of formation of cyclobutyl cation is 225.1 ± 1.1 kcal/mol. The adiabatic IP of cyclobutyl radical (7.54 ± 0.02 eV) is ~.25 eV higher

than would be estimated by considering the IPs of other secondary radicals, such as isopropyl (7.36 ± 0.02 eV)[34], sec-butyl (7.25 ± 0.02 eV)[34], cyclopentyl (7.21 ± 0.02 eV)[43,44] and cyclohexyl (7.15 ± 0.04 eV)[43,44] radicals. The C-H bond dissociation energy of cyclobutane is 1.0 kcal/mol greater than the secondary C-H bond energy in n-butane[11], indicating a small amount of extra energy is needed to form a radical center in cyclobutane compared to other alkanes. The higher adiabatic IP for cyclobutyl radical indicates that even more additional energy is needed to form a cation center in cyclobutane compared to other alkanes. This is reflected in the hydride affinity of cyclobutyl cation, which is ~8 kcal/mol greater than that expected for a secondary C_4 cation (see Figure 10). Using the hydride affinity as a measure of relative cation stabilities, cyclobutyl cation is ~8 kcal/mol less stable than a typical secondary C_4 cation. This may be a somewhat exaggerated estimate of the instability of the cyclobutyl cation, since for all the other secondary radicals, except for isopropyl radical, the photoelectron band onset was chosen as the adiabatic IP, since no vibrational structure could be resolved on these bands. If the photoelectron band onset for cyclobutyl radical (~7.40 eV) is used to estimate the lowest energy cyclobutyl cation formed by photoionization of the radical, then the cyclobutyl cation is ~5 kcal/mol less stable than a typical secondary cation. As will be discussed later in the section on ionic structures, this instability of the cyclobutyl cation is probably a result of its somewhat rigid four-membered ring structure. The peak assigned to the adiabatic IP may also not arise from the 0-0 transition. If Franck-Condon factors are not favorable enough to observe the 0-0 transition, the reported heat of formation of the ion is then an upper limit.

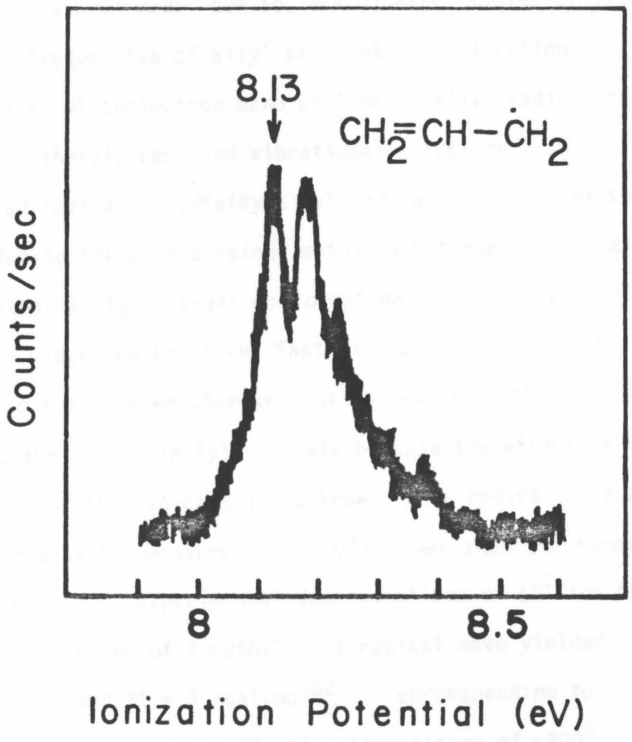
From the photoelectron data, the proton affinity of cyclobutene to form cyclobutyl cation is calculated to be 178.2 kcal/mol. An experimental determination of the proton affinity of cyclobutene yielded a value of 191 kcal/mol[30]. An ICR bracketing technique was used, where it was observed whether a proton transfer reaction with cyclobutene was exothermic or endothermic. No equilibria were established[32]. If a $C_4H_7^+$ cation is being formed at its threshold through the proton transfer reaction, then it has a heat of formation of 212 kcal/mol[31]. A cyclopropylcarbinyl structure for the cation has been suggested[30,32], and was recently supported by the good agreement between STO-3G ab initio calculations[48] of heats of isodesmic reactions involving cyclopropylcarbinyl cation and the experimental values calculated using 212 kcal/mol for the heat of formation of the cation. It cannot correspond to a $C_4H_7^+$ cation with the cyclobutyl cation structure accessed by photoionization of the cyclobutyl radical, which has a heat of formation 11 kcal/mol higher.

Cation Structures. The shape of the first photoelectron band, being determined by Franck-Condon factors between the radical and the cation in their ground electronic states, provides information regarding the relative shapes of the ionic and radical potential energy surfaces in the region of the radical geometry. If adiabatic and vertical IPs coincide, the equilibrium nuclear coordinates of the radical and cation differ little. Vibrational fine structure on the photoelectron band then indicates changes in force constants upon ionization. If the adiabatic and vertical IPs do not coincide, the difference between them indicates the extent to which the equilibrium geometry of the cation differs from that of the radical.

1-Methylallyl radical and 2-methylallyl radical have quite differently shaped first photoelectron bands, although they are both methyl-substituted allyl radicals. 1-Methylallyl radical and cation can take on both trans and cis conformations (V a and b, respectively). The photoelectron spectrum of 1-methylallyl radical is due to ionization of radicals with these two different conformations. The presence and specific location of the methyl substituent on the allylic framework also influences the structural changes which occur upon ionization of the unpaired electron in the radical.

2-Methylallyl radical and both cis and trans conformations of 1-methylallyl radical have been observed and assigned in ESR experiments[49,50]. Their identification as π-conjugated radicals and the specific assignments were made by comparing the spectra with that of allyl radical. Allyl[15], benzyl[15] and cycloheptatrienyl radicals[9c], all π-conjugated radicals, have first photoelectron bands characterized by sharply resolved vibrational structure with the adiabatic and vertical ionization potentials coinciding. The first photoelectron band of 2-methylallyl radical is very similar to these, especially to that of allyl radical shown in Figure 11. However, the adiabatic IP of 2-methylallyl radical is displaced by 0.05 eV from the vertical IP, indicating that the equilibrium geometry of the cation is slightly different from that of the radical. The most obvious difference between 2-methylallyl and these other π-conjugated radicals is the methyl group, which is attached to the conjugated carbon framework. The near coincidence of the frequencies associated with the vibrational structure resolved on the allyl[15] and 2-methylallyl radical photoelectron bands, 420 and 410 cm^{-1},

Figure 11: He I spectrum of allyl radical. Data taken from Reference 15.


8.13
$CH_2=CH-\dot{C}H_2$
Counts/sec
8
8.5
Ionization Potential (eV)

respectively, indicates that movement of the methyl group itself is not involved. However, the presence of the methyl group could influence the equilibrium nuclear conformation in the cation associated with this vibrational mode. No assignment of these vibrational frequencies of the ions has been made due to lack of experimental or calculated vibrational frequencies of allyl or 2-methylallyl cation.

The first photoelectron band of 1-methylallyl radical is broader and has less sharply resolved vibrational structure than the other π-conjugated radicals. 1-Methylallyl radical differs from these other radicals due to the unconstrained methyl substituent which allows it to take either a cis or trans conformation. Since pyrolysis takes place under low-pressure, fast-flow conditions, it is difficult to estimate whether an equilibrium is established between cis- and trans-1-methylallyl radicals because the effective vibrational temperatures of the radicals are unknown. The radicals are probably characterized by temperatures 200-300° C lower than the furnace temperature [43]. Experimental determinations of $\Delta G^{\ddagger}$ for the trans to cis isomerization of 1-methylallyl radical have yielded values of $\leq 14.4 \pm 2$ [51] and 21 ± 3 kcal/mol [52], corresponding to rates of trans to cis isomerization at an effective temperature of ~300° C of 4×10^{7} sec^{-1} and 1×10^{5} sec^{-1}, respectively. If ~300° C is a reasonable average estimate for the temperatures which characterize the radicals formed during the precursor's ~1 msec residence time in a furnace operated at 500-700° C, then it is not unlikely that a near equilibrium is reached in the pyrolyzer and this mixture sampled in the ionization region. This is consistent with the fact that the same 1-methylallyl radical

spectrum is obtained from precursors which initially produce only cis or trans-1-methylallyl radicals. Experimentally, the entropy of trans-1-methylallyl radical is 1.4 ± 2.0 x 10^{-4} kcal/mol-°K greater than that of cis, and the enthalpy of cis-1-methylallyl radical is 0.151 ± 0.060 kcal/mol greater than that of trans[53]. Using these values, and assuming an equilibrium at ~300° C is reached, the ratio of trans to cis-1-methylallyl radical is ~1.2:1.0.

Ab initio calculations on both trans- and cis-1-methylallyl cation indicate that the trans configuration is lower in energy than the cis by 3.0 kcal/mol at the STO-3G level[45] and 3.36 kcal/mol at the STO4-31G level[54]. The radical also prefers to be trans, but only by 0.2 kcal/mol from experimental evidence[53], and by 1.02 kcal/mol from a STO4-31G calculation[54]. From these energy differences, the adiabatic IP of trans-1-methylallyl radical is estimated to be ~0.09-0.14 eV lower than that of cis-1-methylallyl radical. Based upon these studies, the adiabatic IP determined in this work is assigned to the trans isomer.

The much more subtle orientational preference of the methyl rotor about the allylic framework has also been noted in theoretical studies. As determined by STO-3G ab initio calculations[54], the methyl rotor in the trans isomer of the radical and cation prefers to eclipse rather than to stagger the partial double bond of the allylic moiety. Torsional barriers to a staggered form of trans radical and cation are 0.73 and 0.83 kcal/mol, respectively. The methyl group in cis-1-methylallyl cation also prefers an eclipsed conformation, with a 0.57 kcal/mol rotation barrier to a staggered form. However, cis-1-methylallyl radical adopts a staggered conformation with a torsional barrier of only 0.14 kcal/mol. These

slight conformational preferences are not great enough to displace the vertical from the adiabatic IP. However, they may cause excitation of low frequency torsional modes upon ionization, which will tend to wash out or broaden structure that would otherwise be much more sharply resolved.

On ionization of isopropyl and tert-butyl radicals, systems where methyl groups are bound to a radical center, C-C stretching modes are excited[42]. Theoretical calculations[54] on 1-methylallyl radical and cation did not optimize the C-CH_3 bond distance and thus did not examine the changes in this bond distance which may occur on ionization of the radical. However, by comparison with the isopropyl and tert-butyl systems, excitation of the C-CH_3 stretching mode would be expected on ionization of 1-methylallyl radical. This difference in equilibrium geometry between radical and cation could result in the vertical IP being displaced from the adiabatic IP.

Thus, there are several factors which may contribute to producing a first photoelectron band for 1-methylallyl radical which is quite different from those of allyl or 2-methylallyl radical. Both cis and trans spectra may look different from that of the other two allyl radicals due to excitation upon ionization of a low frequency torsional mode and a C-C stretching mode. Overlapping of the cis and trans photoelectron bands may serve to mask some of the structure present on the individual bands, and most likely prevented us from identifying vibrational progressions on the structured band.

ESR data on allylcarbinyl radical show no evidence for significant homoconjugation between the unpaired electron and the π electrons in the double bond. The α and β proton[55] coupling constants are typical of those expected for a primary radical[56]. Selective line

broadening is observed in the allylcarbinyl radical ESR spectrum, due to hindered rotations about the C_α-C_β and C_β-C_γ bonds[57]. From the temperature-dependent β-proton coupling constants, the barrier to rotation about the C_α-C_β bond has been calculated to be 223 cal/mol[58], typical of a primary radical. Although this barrier height may be imprecise[57], ESR evidence seems to indicate that allylcarbinyl radical is a typical primary radical. Theory is also in agreement. An ab initio calculation yielded a barrier to rotation about the C_β-C_γ bond of approximately 2.1 kcal/mol[59]. These results justify our use of a primary C-H bond energy to estimate the heat of formation of allylcarbinyl radical. We would expect that a typical primary ion (IIIa) would be formed on ionization of the radical, not a geometrically constrained, delocalized allylcarbinyl cation (IIIb). The thermochemistry of the allylcarbinyl system supports this.

The first photoelectron band of allylcarbinyl radical is broad and featureless, as is the first photoelectron band of n-butyl radical[34]. n-Propyl radical has a broad photoelectron band, although weak fine structure is resolved on the low ionization potential side of the band[34]. A featureless band for allylcarbinyl radical is not unreasonable, due to excitation of several vibrational and torsional modes on ionization. Absence of a local minimum on the $C_4H_7^+$ potential surface for allylcarbinyl cation could also result in a smooth photoelectron band. If photoionization forms an ion on a descending part of a very broad potential energy surface, vibrational states may be so closely spaced as to result in a smoothly varying photoelectron band.

ESR data have been interpreted to indicate that in solution cyclobutyl radical has a planar[56,60] or "essentially" planar[61], radical center since

its α-proton hyperfine splitting is similar to a value characteristic of a π-electron radical center and to those of other secondary radicals. A small degree of nonplanarity in its equilibrium conformation cannot be ruled out since there is a question as to whether acyclic alkyl radicals are planar or slightly nonplanar[42]. The equivalence of the four β protons and the value of their isotropic hyperfine coupling constant suggest that the ring is planar as well[56]. An INDO calculation[60] of the average β-proton coupling constants in cyclobutyl radical was done as a function of the amount of ring puckering for a planar radical center. The experimentally observed coupling constant could only be predicted using a rigid planar ring, where the β protons are equivalent by symmetry, or for a ring rapidly oscillating between two structures that are very nearly planar. The effect of a slightly nonplanar radical center was not investigated.

Semiempirical calculations of cyclobutyl cation have disagreed as to whether the planar or puckered system is more stable[62-65]. In cases where the puckered ring is more stable, substantial 1,3 carbon/carbon cross-ring bonding interactions are shown to contribute special stability to the system[63,64]. Ab initio molecular orbital calculations predict that puckered cyclobutyl cation is not at a minimum on the ionic potential surface[13]. Several experimental results described in the Introduction, in particular the kinetic energy release measurements of dissociating $(C_4H_7\ Br)^+$ ions[6], indicate that cyclobutyl cation does exist in a potential well in the gas phase.

The general shapes and breadths of the cyclobutyl, cyclopentyl, and cyclohexyl radical[43,44] photoelectron spectra are similar. Since adiabatic and vertical IPs do not coincide, the equilibrium geometry of each ion differs from that of the corresponding radical. From Table III we see that the vertical IPs are displaced only ~.25 eV from the photo-

Table III. Comparison of the First Photoelectron Bands of Cyclic and Acyclic Secondary Radicals[a]

R	Band Onset	Vertical IP	Vertical IP - Onset
C-C_4H_7	~7.40	7.66	~0.26
C-C_5H_9	7.21	7.46	0.25
C-C_6H_{11}	7.15	7.40	0.25
iso-C_3H_7	7.36	7.69	0.33
sec-C_4H_9	7.25	7.59	0.34

a. All quantities in eV. Cyclobutyl data from this work. Cyclopentyl and cyclohexyl data from Refs. 43 and 44. Isopropyl and sec-butyl data are taken from Refs. 15 and 34, respectively.

electron band onsets in these cyclic systems where both radical and ion are fairly constrained as compared to ~.33 eV for the secondary acyclic systems. Whereas cyclopentyl and cyclohexyl radical bands are featureless, structure due to vibrational excitation is clearly resolved on the cyclobutyl radical band. Explanations given[44] for the absence of structure on the cyclopentyl and cyclohexyl radical photoelectron bands also apply to a comparison between these two cyclic radicals and cyclobutyl radical. Lack of structure may be due to the overlapping of bands arising from ionization of low-lying nondegenerate conformations of the cyclopentyl or cyclohexyl radicals. These radical conformations have been identified in ESR experiments, but ESR experiments on cyclobutyl radical indicate the radical is only in one conformation or possibly rapidly interconverting between degenerate conformations. Excitation of very low frequency vibrations on ionization may also tend to mask structure that would otherwise be observable. The larger, less rigid systems such as cyclopentyl and cyclohexyl radicals, as compared to cyclobutyl radical, would be most likely to manifest this. Finally, absence of structure may be an indication that the ion is not stable with respect to isomerization, resulting in excitation of very closely spaced vibrational states. Therefore, the presence of structure on the cyclobutyl radical band is consistent with cyclobutyl cation being at a local minimum on the $C_4H_7^+$ potential energy surface, as indicated by experiments[6-8].

The resolved vibrational progression on the cyclobutyl radical photoelectron spectrum, characterized by a frequency of 990 ± 100 cm^{-1}, has not been assigned. Those vibrations corresponding most closely to the change in equilibrium geometry caused by ionization will be most strongly excited. Since the ring of the radical is planar or nearly so, according

to ESR data, and the majority of theoretical calculations assign special stability to cross-ring interactions in cyclobutyl cation, a ring-puckering mode may be excited. However, it probably would not be resolved in the photoelectron spectrum of cyclobutyl radical since the ring-puckering mode in cyclobutane has a frequency of 200 cm^{-1} [66]. Ring-deformation modes may also be excited. In cyclobutane, ring-deformation modes involve C-C stretching, C-C-C bending and CH_2 deformation and have frequencies of ~1000 cm^{-1}. An assignment is also suggested by consideration of the photoelectron spectrum of another secondary radical, that of isopropyl radical[42]. A resolved progression of 970 cm^{-1} on the first photoelectron band of isopropyl radical was assigned to a mixed, totally symmetric C-C stretching, HCC bending (at the CH_3 groups) mode of the ion. If the geometry changes occurring upon ionization of cyclobutyl radical are similar to those occurring at the isopropyl radical center, then the 990 cm^{-1} vibrational progression may arise from excitation of an analogous skeletal deformation mode of cyclobutyl cation, which would be similar to the ring-deformation modes in cyclobutane.

As mentioned in the section on ion thermochemistry, the adiabatic IP of cyclobutyl radical corresponds to formation of an ion that is less stable, by 5 to 8 kcal/mole than would be predicted for a C_4 secondary cation, based on the hydride affinities of acyclic and cyclopentyl and cyclohexyl cations. The difference between the band onset and vertical IP for cyclobutyl radical is nearly the same as for cyclopentyl and cyclohexyl radicals (see Table III). Thus, cyclobutyl cation achieves the same amount of stabilization, by small deviations from the equilibrium radical geometry, as do cyclopentyl and cyclohexyl cations, which appear to be normal secondary cations as indicated by their hydride affinities.

One possible explanation for the higher adiabatic (and vertical) IP for cyclobutyl radical than would be expected for a typical C_4 secondary radical derives from a consideration of the effect of the strained four-membered ring system on the radical center. Slower rates of hydrogen abstraction from cyclobutane and the stronger C-H bond in cyclobutane, compared to cyclopentane and cyclohexane, have been explained by a small increase in the s-character of the C-H bonds in cyclobutane[64]. The carbon hybrid orbitals which form the ring C-C bonds have more p character than pure sp^3 hybrids, to minimize strain in the ring, and thus the carbon orbitals participating in the C-H bonds have more s character. If the unpaired electron in cyclobutyl radical also occupies an orbital with more s character than other secondary radicals, it is more strongly bound and thus the energy to ionize it is greater. If this explanation is correct, the ESR α-proton coupling constant is not sensitive to the (probably small) increased nonplanarity at the cyclobutyl radical center compared to other secondary radical centers. The cation formed by photoionization of the radical is less stable than a typical secondary ion because the planar configuration preferred by a cation center is opposed by the nonplanar center preferred by the four-membered ring. The puckered cyclobutyl cation, with its extremely nonplanar cation center, may be a more stable conformation of the cyclobutyl cation. However, Franck-Condon factors for transition to this structure of the cation from the radical would be very small.

Radical Thermal Decomposition and Isomerization. By photoelectron spectroscopy, both reactive intermediates and stable species may be directly observed, so that products of radical pyrolysis may be identified[43,44].

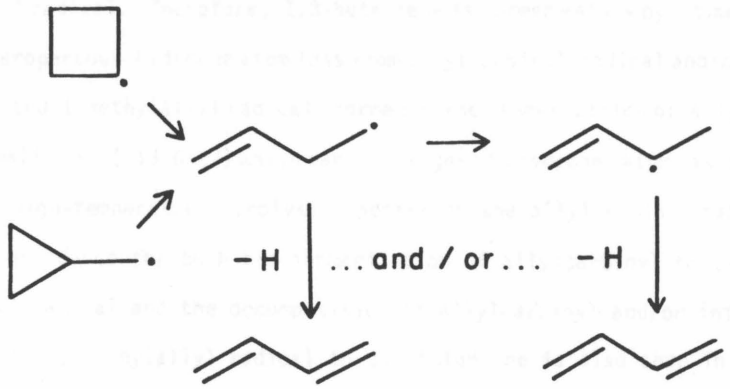
Overlapping photoelectron spectra may obscure some products so that in general only the major products can be identified clearly. Those species with lifetimes ~1 msec can be observed.

A simple scheme, presented in Figure 12, can account for all the products identified in the pyrolysis spectra of 1-methylallyl, allylcarbinyl, cyclobutyl and cyclopropylcarbinyl radicals. 2-Methylallyl radical neither isomerizes to any other C_4H_7 radical, nor is it a product of their isomerization reactions. The radical recombination products tentatively identified in the 1- and 2-methylallyl radical pyrolysis spectra are not included in this scheme. A diagram of the energetics for the unimolecular radical rearrangements and decomposition reactions is included in Figure 9. As noted in the experimental section, some of these reactions may in fact take place on the pyrolyzer wall.

Both 1- and 2-methylallyl radical are very stable. No major radical decomposition or isomerization products are seen in the pyrolysis spectra of 2-methylallyl radical, and only a small amount of 1,3-butadiene and/or 2-butene is observed at high temperatures in the pyrolysis spectra of 1-methylallyl radical.

At the lowest temperature at which the nitrite precursor of allylcarbinyl radical decomposes to form this initial radical, both 1-methylallyl radical and 1,3-butadiene are formed. The isomerization of allylcarbinyl radical to 1-methylallyl radical has been proposed to account for the products of radical scavenging in chemically and thermally activated radical decompositions[68-70]. An activation energy of 20.0 ± 0.7 kcal/mol was determined for the thermal radical isomerization[68,70]. The best agreement between rate constants calculated by RRKM theory applied to a 1,2-H shift mechanism and experimental rate constants obtained in chemical

Figure 12: Major thermal decomposition and isomerization pathways for C_4H_7 radicals as observed by photoelectron spectroscopy.


-H
... and / or ...
-H

activation studies was found when the threshold energy is 33.0 kcal/mol and log A(sec^{-1}) is 12.68[69]. Other mechanisms, such as a 1,3-H shift, were not considered. 1,3-Butadiene is the other thermolysis product of allylcarbinyl radical. Production of 1,3-butadiene in the high-pressure experiments, where radical scavenging techniques are used, is accounted for by disproportionation reactions involving allylcarbinyl or 1-methyl-allyl radical[69,71,72]. The other products of disproportionation reactions, 1-butene and 2-butene, are not observed in the photoelectron spectra. A small amount of what may be 1,3-butadiene is observed in the pyrolysis spectra of 1-methyl-allyl radical. Therefore, 1,3-butadiene is formed mainly by unimolecular or heterogeneous hydrogen atom loss from allylcarbinyl radical and/or internally excited 1-methylallyl radical, formed by the isomerization of allylcarbinyl radical. A small peak (~13.6 eV) which can be assigned to hydrogen atoms is observed in the high-temperature pyrolysis spectra of the allylcarbinyl radical precursor.

Evidence for both the isomerization of allylcarbinyl to 1-methyl-allyl radical and the decomposition of allylcarbinyl and/or internally excited 1-methylallyl radical to 1,3-butadiene is also seen in the pyrolysis spectra of the cyclobutyl and cyclopropylcarbinyl radical precursors. Ring opening of cyclobutyl radical to allylcarbinyl radical has been studied by chemical and thermal activation of cyclobutyl radical. With the exception of one determination of 18.1 kcal/mol[68], values for the activation energy for ring opening of cyclobutyl radical fall in the range of 27-35 kcal/mol[71,73,74]. It is possible to observe the cyclobutyl radical in photoelectron spectra under nearly the same pyrolysis conditions as those required for cyclopentyl and cyclohexyl radicals[43], whose activation energies for ring opening are 31 kcal/mol

and 31-37 kcal/mol, respectively[71]. It is not likely, then, that the activation energy for ring opening of cyclobutyl radical is very different from these values.

The ring-opened product, allylcarbinyl radical, is not observed in the pyrolysis spectra of the cyclobutyl radical precursor. Allylcarbinyl radical presumably isomerizes or decomposes rapidly, since it is born with ~33 kcal/mol internal energy (see Figure 9). 1-Methylallyl radical and 1,3-butadiene are the major products of cyclobutyl radical thermolysis via the allylcarbinyl radical intermediate.

Ring opening of cyclopropylcarbinyl radical to allylcarbinyl radical has been extensively investigated in recent years[75]. Although this unimolecular reaction is extremely rapid, its rate has been measured in solution by EPR spectroscopy[29]. An activation energy of 5.94 ± 0.57 kcal/mol and a log A(sec^{-1}) of 12.43 ±0.85 were determined. No evidence for cyclopropylcarbinyl radical was observed in photoelectron spectra of the pyrolysis products of the precursor to this radical. This was to be expected for a radical with such a rapid unimolecular decomposition reaction.

The ring-opened product, allylcarbinyl radical, is observed. Combining the heats of formation of cyclopropylcarbinyl radical (51.6 kcal/mol[33]) and allylcarbinyl radical with the activation energy for ring opening of cyclopropylcarbinyl[29], we can estimate that the allylcarbinyl radical is born with 12 ± 3 kcal/mol internal energy (see Figure 9). This is consistent with the activation energy (9.0 kcal/mol[76]) for the reverse reaction, allylcarbinyl radical ring closing to cyclopropylcarbinyl radical (see below). The isomerization product of

allylcarbinyl radical, 1-methylallyl radical, and 1,3-butadiene are also observed in the pyrolysis spectra of the cyclopropylcarbinyl radical precursor.

Allylcarbinyl radical can ring close to cyclopropylcarbinyl radical, but no evidence has been found for formation of cyclobutyl radical from allylcarbinyl radical[77]. The rate of allylcarbinyl ring closure to cyclopropylcarbinyl has been determined by NMR and EPR spectroscopy[76]. These experiments yielded an activation energy of 9.0 ± 0.5 kcal/mol and a log A(sec^{-1}) of 10.3 ±0.5 for this unimolecular reaction. By combining this rate with the rate of cyclopropylcarbinyl radical ring opening[29], the relative concentrations of allylcarbinyl to cyclopropylcarbinyl radical under equilibrium conditions at 300° C (an average effective pyrolysis temperature) is ~2 x 10^3. Thus, we would not expect to observe cyclopropylcarbinyl radical in the photoelectron spectra of C_4H_7 radical pyrolysis products due to ring closing of allylcarbinyl radical.

Commentary

The results presented here, in conjunction with the results of other investigations, offer a basis for further studies of the structural identities, corresponding heats of formation and interconversion pathways of the $C_4H_7^+$ species. Appearance potential measurements for $C_4H_7^+$ fragment ions strongly suggest that an upper limit for the heat of formation of the most stable gas-phase $C_4H_7^+$ ion(s) is 206 ± 2 kcal/mol[4,10]. This coincides, within experimental error, with the heat of formation of 1-methylallyl cation determined in that work (204 ± 3) and in the present study (203.1 ± 1.4 kcal/mol). Other structures may be equally stable. The heats of formation of puckered cyclobutyl cation and bicyclobutonium cation are not

known, and only a tentative heat of formation for cyclopropylcarbinyl cation (212 kcal/mol[30,31]) has been proposed. Theoretical studies[13] and NMR experiments under stable-ion conditions[2] indicate that these species are all very close in energy. The slightly puckered cyclobutyl cation is a higher-energy species; its heat of formation (225.1 ± 1.1 kcal/mol) was determined in this work. A determination of the ionization potential of cyclopropylcarbinyl radical, providing a definitive value for the heat of formation of cyclopropylcarbinyl cation, would greatly further an understanding of the $C_4H_7^+$ system in the gas phase. Producing the radical by pyrolysis is not the method of choice, as was confirmed in this work. Photolysis of an appropriate precursor would allow more control over the ambient temperature and the distance between radical production and the ionization region.

Recently, the first equilibrium between an allyl and a cyclopropylcarbinyl cation was observed under stable-ion conditions[78]. Cis-1-methylcyclopropylcarbinyl cation rearranges at -100 °C to 1-ethylallyl cation. However, interconversion between the parent cyclopropylcarbinyl (or bicyclobutonium) cation and 1-methylallyl cation has not been observed in solution. 1-Methylallyl cation[3] and bicyclobutonium cation[2c] are stable up to -20° and -60° C, respectively, under stable-ion conditions. Continuation of the experiments to higher temperatures resulted in decomposition reactions of the cations. Significant barriers must exist to prevent the interconversion. For comparison, the rearrangement of sec-butyl cation to the more stable tert-butyl cation has been observed to take place at a significant rate only above ~-40° C[79]. The activation energy for this process, assuming a normal log A, was estimated to be ~18 kcal/mol. In the gas phase, sec-butyl cation can also survive without rearrangement to tert-butyl

cation[80]. Similarly, the significant barrier to interconversion of bicyclobutonium and 1-methylallyl cations under stable conditions may allow separate preparation of the isomers and their rearrangement pathways to be studied in the gas phase or in matrix isolation experiments where competing side reactions may be avoided.

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CHAPTER III

Photoelectron Spectroscopy of 1-Propyl, 1-Butyl, Isobutyl, Neopentyl and 2-Butyl Radicals: Free Radical Precursors to High-Energy Carbonium Ion Isomers.

Photoelectron Spectroscopy of 1-Propyl, 1-Butyl, Isobutyl, Neopentyl and 2-Butyl Radicals: Free Radical Precursors to High Energy Carbonium Ion Isomers

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Abstract

The first photoelectron bands of 1-propyl, 1-butyl, isobutyl, neopentyl and 2-butyl radicals have been obtained. Adiabatic and vertical ionization potentials, respectively, are 8.15 ± 0.02 and 8.43 ± 0.02 eV for 1-propyl radical, 8.02 (+0.04 - 0.1) and 8.50 ± 0.04 eV for 1-butyl radical, 7.93 (+0.03 - 0.1) and 8.31 ± 0.03 eV for isobutyl radical, 7.88 ± 0.05 and 8.25 ± 0.03 eV for neopentyl radical, and 7.25 ± 0.02 and 7.59 ± 0.03 eV for 2-butyl radical. Using recently determined or estimated heats of formation of the radicals, heats of formation of the corresponding carbonium ions are calculated to be 210.5 ± 1.1 kcal/mol for 1-propyl cation, 201.9 ± 3 kcal/mol for 1-butyl cation, 197.9 ± 3 kcal/mol for isobutyl cation, 188.8 ± 2.3 kcal/mol for neopentyl cation and 181.0 ± 1.1 kcal/mol for 2-butyl cation. These values are compared to reaction energetics and thermochemical quantities, measured in the gas phase and solution, which involve formation of 2-butyl cation or have been proposed to relate to the formation of one of the primary ions. With the exception of the 1-propyl radical spectrum, the spectra exhibit no resolved vibrational structure. The possible origins of a weakly resolved 540 ± 160 cm^{-1} vibrational progression observed on the 1-propyl radical band are discussed. Analyzing these spectra, along with those of ethyl and 2-propyl radicals, reveals trends in ionization potentials which may be interpreted in terms of inductive and hyperconjugative effects of methyl substituents beta to primary or secondary cation centers.

Introduction

Carbonium ions have a great tendency, in the gas phase[1] and in solution[2], to rearrange. The lowest-energy isomer is often well characterized by spectroscopic studies of stable ion solutions[3], by calorimetric measurements[4], and by gas-phase studies of ion fragmentation thresholds[5] and ion-molecule reactions[6]. Higher-energy isomers are usually much more elusive and thus poorly characterized.

The present study is an extension of our use of photoelectron spectroscopy of 2-propyl and tert-butyl radicals to examine the most stable propyl and butyl carbonium ions, 2-propyl and tert-butyl cations[7]. To study the higher-energy carbonium ion isomers, the first bands of the photoelectron spectra of 1-propyl, 1-butyl, isobutyl and 2-butyl radicals have been obtained. To complete the series in which the β-hydrogens of the ethyl radical are successively replaced with methyl groups, we have also studied the neopentyl radical. Photoelectron band shapes are governed by Franck-Condon factors, and thus the photoelectron spectrum of a radical contains thermochemical and structural information about the cation, in a specific electronic state, with a geometry similar to that of the radical. Any isomerization of the cation subsequent to ionization will not complicate the data since it is only the ejected electron that is analyzed. Examination of the ionization energetics of 1-propyl, 1-butyl, isobutyl, neopentyl and 2-butyl radicals has yielded the heats of formation of 1-propyl, 1-butyl, isobutyl, neopentyl and 2-butyl cations, respectively, in their ground electronic states. Trends in ionization potentials have been interpreted in terms of inductive and hyperconjugative stabilization available to the ions in their nascent conformations.

Photoelectron spectroscopy of primary radicals offers a unique opportunity to study the primary cations. Theoretical and experimental evidence suggests that primary alkyl cations are extremely transient species. The most detailed ab initio molecular orbital calculations[8] and semiempirical calculations[9,10] failed to determined a minimum on the $C_3H_7^+$ potential energy surface corresponding to 1-propyl cation. The majority of gas-phase experiments have revealed that 1-propyl, 1-butyl, isobutyl and neopentyl cations isomerize either to a protonated cycloalkane or to a more stable secondary or tertiary isomer much more rapidly than they react[1a,11-15]. Attempts to trap 1-propyl cation, for example, have shown that it rearranges in less than 10^{-10} sec[1a,11]. Accurate heats of formation of the primary cations studied in this work cannot be obtained by measuring thresholds for appearance of fragment ions[5] because isomerization of the precursor ion can occur either before or during dissociation[16,17]. The threshold then corresponds to formation of a more stable isomer[5b,18]. Attempts to prepare primary cations under stable-ion conditions for observation by NMR have been unsuccessful[19]. Deamination reactions are often used in solution to generate "free" cations which are characterized by their extensive rearrangement products[20]. Detailed studies using primary amines have revealed that the unrearranged primary products are not formed from totally free carbonium ion intermediates[21], and thus the observation of such products may offer little information concerning the stability of truly free gas-phase primary cations.

Obtaining the photoelectron spectrum of 2-butyl cation completes our study of the $C_4H_9^+$ species which have radical-like structures. 2-Butyl cation has been studied previously in both stable-ion media and in the gas phase, since there is a significant barrier to rearrangement

to its more stable isomer, tert-butyl cation[11,12,22]. Nevertheless, even in a matrix at -190 °C, 2-butyl cation is not a static secondary cation[23]. Olah[24], Saunders[25] and their co-workers have proposed that an equilibrium between a static nonclassical bridged species and a classical secondary cation, both close in energy, accounts for the NMR data on 2-butyl cation.

With the foundation of photoelectron spectroscopic studies of alkyl radicals such as methyl, ethyl, 2-propyl and tert-butyl[7], where both the radical and cation have been well characterized, less well understood systems such as those studied here can be examined. The spectra of the primary and 2-butyl radicals must be assigned correctly. This is assured since the spectra of the more stable secondary or tertiary radicals, which are possible rearrangement products of the radicals themselves, have been obtained previously, or in this work or can be predicted. In addition to obtaining the spectra, photoelectron spectroscopy can be used to follow the thermal decomposition or isomerization pathways of the radicals by identifying the spectra of products[26]. The first photoelectron bands of those alkyl radicals larger than methyl which have been studied previously do not have coinciding adiabatic and vertical ionization potentials[7]. The spectra obtained in this study would also be expected to have some breadth, reflecting changes in the equilibrium geometry in going from the radical to the ion. Previous studies[7] also indicate that if vibrational structure is resolved, it would be expected to be weak due to excitation upon ionization of several vibrational modes.

Experimental Section

Photoelectron spectra were recorded on a spectrometer of standard design, which has been specifically modified to study products of gas-phase pyrolysis. It has been described in detail elsewhere[27].

1-Propyl, 1-butyl, isobutyl, neopentyl and 2-butyl radicals were produced by thermal decomposition of 1-butyl nitrite, 1-pentyl nitrite, 3-methyl-1-butyl nitrite, 3,3-dimethyl-1-butyl nitrite and 2-methyl-1-butyl nitrite, respectively, according to reactions 1 and 2. The

$$RCH_2ONO \longrightarrow RCH_2O + NO \qquad (1)$$

$$RCH_2O \longrightarrow R + CH_2O \qquad (2)$$

nitrites were prepared using standard procedures[28] from the corresponding alcohols obtained from Aldrich: 1-butanol, 1-pentanol, 3-methyl-1-butanol, 3,3-dimethyl-1-butanol and 2-methyl-1-butanol, respectively. Pyrolyses were performed over the range 470-650 °C using a 2.2 cm long pyrolyzer. Since the pyrolyses are done at low pressures (~10^{-2} torr), molecules are heated by collisions with the wall of the pyrolyzer and there are few molecule-molecule collisions. Some unimolecular radical processes may, in fact, take place on the pyrolyzer wall. In an attempt to decrease the amount of secondary products and thereby increase the spectrum of the desired radical, a shorter pyrolyzer (0.8 cm) was used for some experiments. Regardless of which pyrolyzer was used, the hot gases traversed a 0.75 cm path after exiting the pyrolyzer and before intersecting the photon beam. Pyrolysis temperatures ~110-180 °C higher were necessary with the short pyrolyzer to obtain the same amount of precursor decomposition achieved with the long pyrolyzer. Spectra showing the same amount of precursor

decomposition were compared, and no increase of the primary radical products nor decrease in the secondary radical products, relative to the amount of nitrite decomposition, was apparent. There is also no evidence that the slightly higher pyrolysis temperatures change the shapes of the radical spectra (due to a temperature-dependent population of radical conformations or higher vibrational states). In particular, no hot bands were observed. We report the best spectra obtained with both pyrolyzers. Unless otherwise specified, pyrolysis temperatures refer to those for the long pyrolyzer.

Spectra were recorded using He I and in some cases Ne I radiation in order to determine those spectral features arising from the He Iβ ionization. Energy scales for the pyrolysis spectra were calibrated using the peaks due to NO and CH_2O, both products of the nitrite decomposition. Room-temperature spectra were calibrated using argon or xenon. Resolution for these experiments was 30-40 meV. Count rates at the radical band maxima for 1-propyl, 1-butyl, isobutyl, neopentyl and 2-butyl radicals were ~26, 18, 27, 13 and 13 sec^{-1}, respectively. Ionization potentials reported here are the average of several determinations. Reasonable estimates for the error involved in assigning an ionization potential (IP) to an identifiable part of a radical spectrum are ± 0.02 or 0.03 eV. In some cases it was necessary to choose an adiabatic IP for a photoelectron band with a slowly rising onset both obscured by another band, probably due to secondary radical products, and without vibrational structure. In this case, and when a vertical IP was chosen for a very broad band maximum, larger errors were assigned to the value.

Results

The ionization potentials measured in this work and, for comparison, values determined previously by electron impact using an energy-resolved electron beam[18,29a] are presented in Table I.

Nitrites. The photoelectron spectra of 1-butyl nitrite, 1-pentyl nitrite, 3-methyl-1-butyl nitrite, 3,3-dimethyl-1-butyl nitrite and 2-methyl-1-butyl nitrite are shown in Figure 1. The vertical IPs of these species are 10.4, 10.6, 10.6, 10.6 and 10.5 eV, respectively.

1-Propyl Radical. The Ne I spectrum of the first photoelectron band of 1-propyl radical is shown in Figure 2. The nitrite precursor was pyrolyzed at 615 °C using the short pyrolyzer. At this temperature (corresponding to ~475 °C with the long pyrolyzer) the radical band is maximized, and small amounts of radical decomposition products are observed. The adiabatic and vertical IPs are 8.15 ± 0.02 and 8.43 ± 0.02 eV, respectively. The adiabatic IP is in good agreement with previous electron impact values of 8.10 ± 0.05 eV[18] and 8.13 ± 0.05 eV[30] and a photoionization mass spectrometric estimate of $\leq$ 8.1 eV[31].

With a He I lamp, the maximum of the radical band is at 8.37 ± 0.02 eV. Although a change in photoelectron band shape with lamp radiation energy cannot be ruled out, the apparent change in vertical IP is probably due to an impurity line in the He I lamp. Ionization of CH_2O by the He Iγ line, which is 2.524 eV more energetic than the main He Iα line, would result in a photoelectron peak with an apparent IP of 8.360 eV. The He Iγ line is only 0.5% of the He Iα intensity, but given the low intensity radical band and the high intensity CH_2O He Iα peak, this impurity line is sufficiently intense to change the apparent vertical IP.

Table I. Summary of Alkyl Radical Ionization Potentials

R	Ionization Potential (eV) by Photoelectron Spectroscopy[a]		Ionization Potential (eV) by Electron Impact[b]
	Adiabatic	Vertical	
CH_3	9.84 ± 0.02	9.84 ± 0.02	9.84 ± 0.03
CH_3CH_2	8.39 ± 0.02	8.51 ± 0.02	8.38 ± 0.05
2-C_3H_7	7.36 ± 0.02	7.69 ± 0.02	7.55 ± 0.05
t-C_4H_9	6.70 ± 0.03	6.92 ± 0.03	6.93 ± 0.05
1-C_3H_7	8.15 ± 0.02	8.43 ± 0.02	8.10 ± 0.05
iso-C_4H_9	7.93(+0.03 - 0.1)	8.31 ± 0.03	8.01 ± 0.05
neo-C_5H_{11}	7.88 ± 0.05	8.25 ± 0.03	7.91 ± ?
1 - C_4H_9	8.02(+0.04 - 0.1)	8.50 ± 0.04	8.01 ± 0.05
2-C_4H_9	7.25 ± 0.02	7.59 ± 0.03	7.41 ± 0.05

[a] From this work except for CH_3, CH_3CH_2, 2-C_3H_7 and t-C_4H_9 from Ref. 7.

[b] Values were obtained using an energy-resolved electron beam from Ref. 18 except for neo-C_5H_{11} from Ref. 29a.

Figure 1. He I spectra of (a) 1-butyl nitrite, (b) 1-pentyl nitrite, (c) 3-methyl-1-butyl nitrite, (d) 3,3-dimethyl-1-butyl nitrite, (e) 2-methyl-1-butyl nitrite.

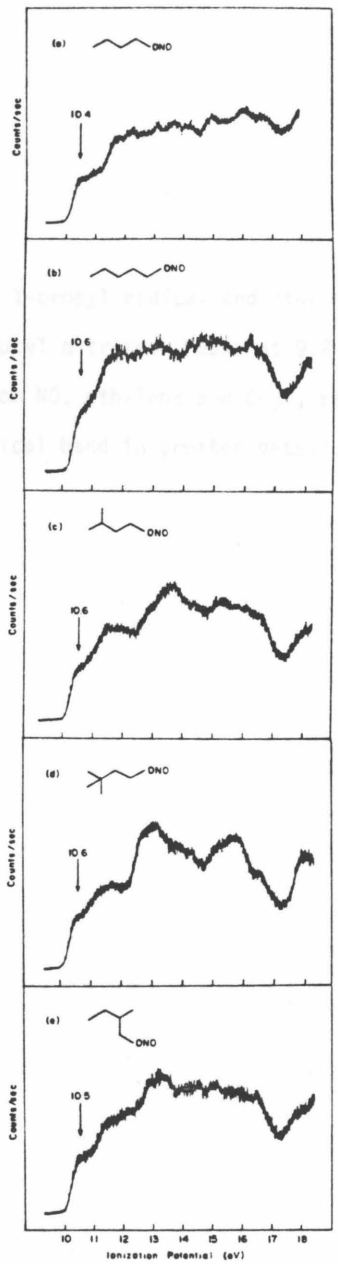
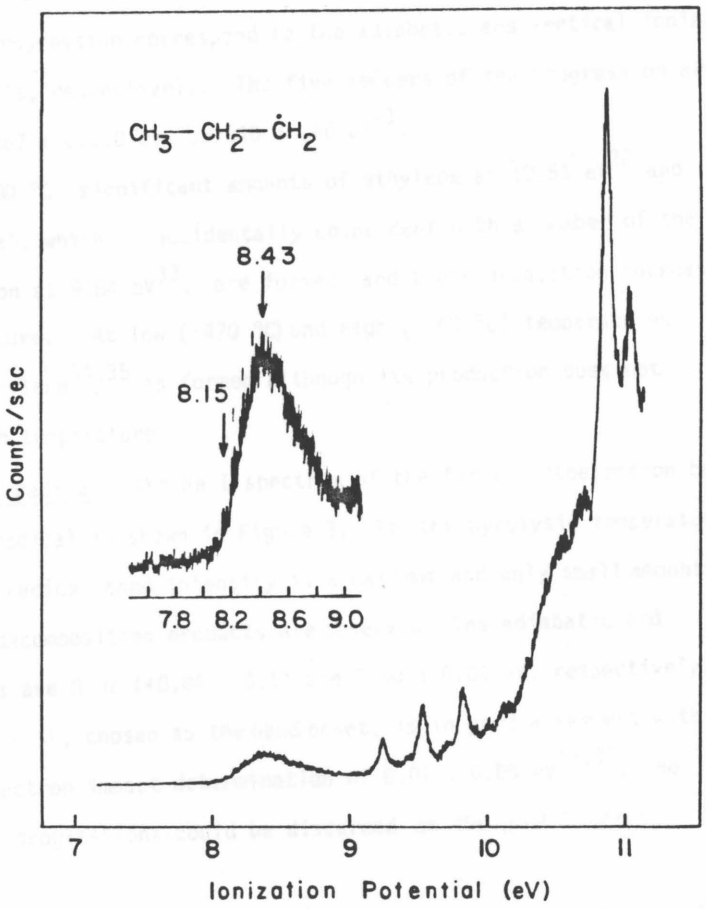

(a)
ONO
10.4
Counts/sec
(b)
ONO
10.6
Counts/sec
(c)
ONO
10.6
Counts/sec
(d)
ONO
10.6
Counts/sec
(e)
ONO
10.5
Counts/sec
10 11 12 13 14 15 16 17 18
Ionization Potential (eV)

Figure 2. Ne I spectrum of 1-propyl radical and other products of the pyrolysis of 1-butyl nitrite. Peaks at 9.2-10, 10.5 and 10.9 eV arise from NO, ethylene and CH_2O, respectively. Insert shows radical band in greater detail.


CH3— CH2—ĊH2
8.43
8.15
7.8 8.2 8.6 9.0
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

Therefore, only the Ne I spectrum was used to assign the vertical IP.

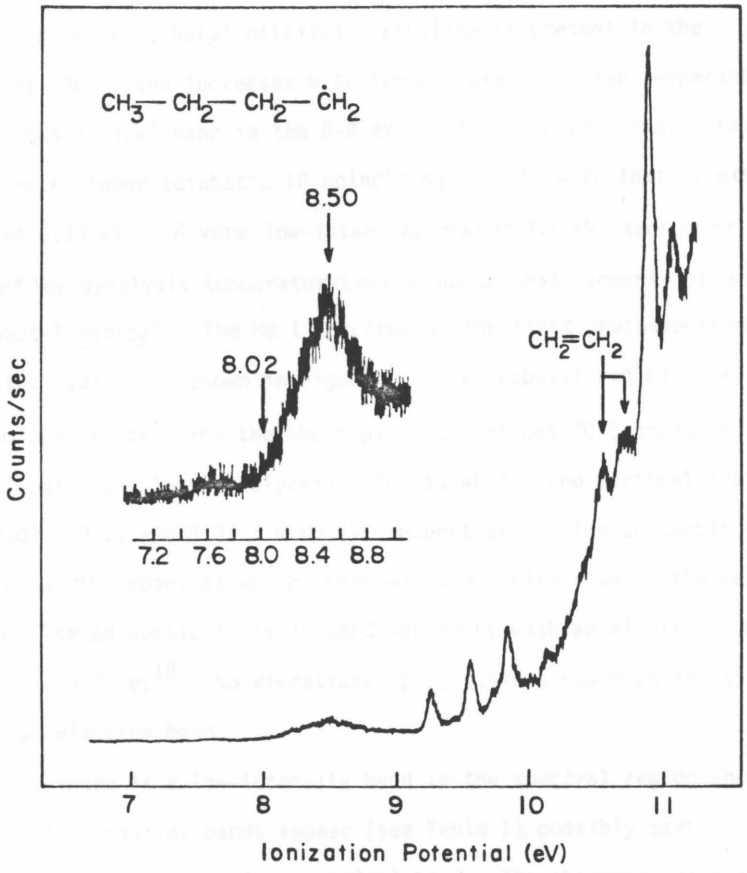
A weakly resolved vibrational progression is just barely evident on the low ionization potential side of the band. The first and fifth peak of the progression correspond to the adiabatic and vertical ionization potentials, respectively. The five members of the progression are spaced by 0.067 ± 0.020 eV, or 540 ± 160 cm^{-1}.

Above 500 °C significant amounts of ethylene at 10.51 eV[32] and methyl radical, which is accidentally coincident with a member of the NO progression at 9.84 eV[33], are formed, and their production increases with temperature. At low (~470 °C) and high (~640 °C) temperatures a little propylene[34,35] is formed although its production does not increase with temperature.

1-Butyl Radical. The Ne I spectrum of the first photoelectron band of 1-butyl radical is shown in Figure 3. At the pyrolysis temperature of 500 °C, the radical band intensity is a maximum and only small amounts of radical decomposition products are observed. The adiabatic and vertical IPs are 8.02 (+0.04 - 0.1) and 8.50 ± 0.04 eV, respectively. The adiabatic IP, chosen as the band onset, is in good agreement with a previous electron impact determination of 8.01 ± 0.05 eV[18,30]. No vibrational progressions could be discerned on the photoelectron band.

The very low intensity band just before that of 1-butyl radical is in the spectral region where the first photoelectron bands of secondary alkyl radicals appear (see Table I). The low signal-to-noise precludes any definite assignment. The observed adiabatic and vertical IPs for this band, ~7.3 and ~7.6 eV, respectively, are, however, consistent with

Figure 3. Ne I spectrum of 1-butyl radical and other pyrolysis products of 1-pentyl nitrite. Peaks at 9.2-10, 10.5 and 10.9 eV arise from NO, ethylene and CH_2O, respectively. Insert shows 1-butyl radical band in greater detail. The very weak band just before the 1-butyl radical band is assigned to a secondary radical, possibly 2-butyl radical.

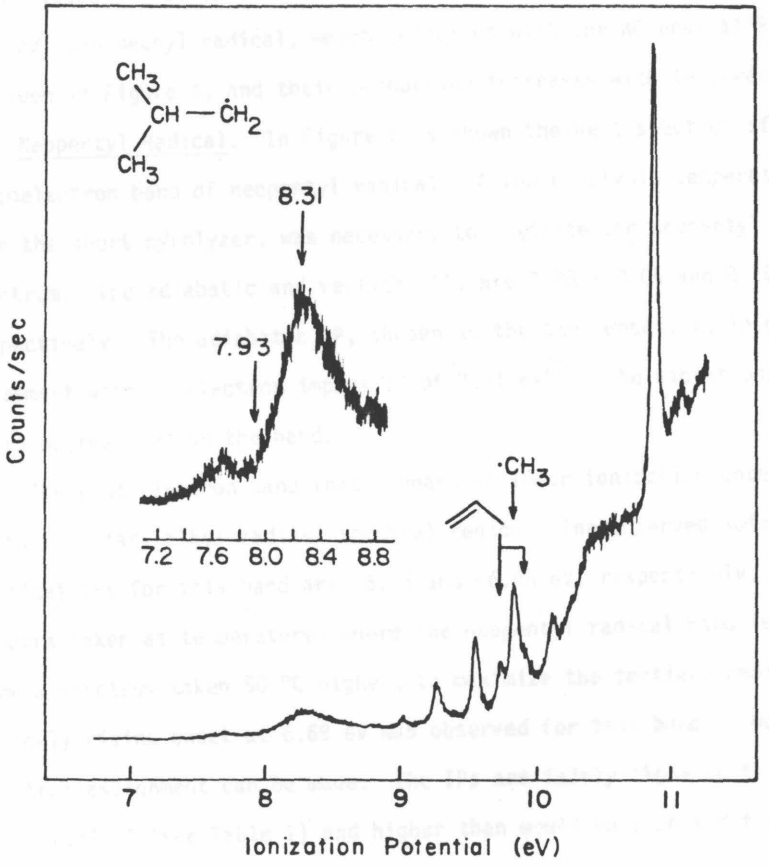

CH3— CH2— CH2— ĊH2
8.50
8.02
CH2=CH2
7.2 7.6 8.0 8.4 8.8
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

those of 2-butyl radical. The intensity of this band does not appear to increase with temperature. The 1-butyl radical precursor sample was checked for purity and found to contain no (<3%)[36] 2-butyl radical precursor (2-methyl-1-butyl nitrite). Ethylene is present in the spectrum at 500 °C and increases with temperature. At high temperatures (~625 °C) the radical band in the 8-9 eV spectral region changes shape, having a much higher adiabatic IP coinciding closely with that of ethyl radical at 8.39 eV[7]. A very low-intensity peak at 9.7 eV, seen in He I spectra at high and low pyrolysis temperatures may be due to small amounts of propylene.

Isobutyl Radical. The He I spectrum of the first photoelectron band of isobutyl radical is shown in Figure 4. The isobutyl radical spectrum was maximized by operating the short pyrolyzer at 685 °C (corresponding to ~500 °C with the long pyrolyzer). The adiabatic and vertical IPs are 7.93 (+0.03 - 0.1) and 8.31 ± 0.03 eV, respectively. The adiabatic IP was chosen as the point at which there was a definite rise in the radical spectrum. The adiabatic IP is in good agreement with an electron impact IP of 8.01 ± 0.05 eV[18]. No vibrational progressions could be identified on the photoelectron band.

Again, there is a low-intensity band in the spectral region where secondary alkyl radical bands appear (see Table I), possibly partially obscuring the onset of the primary radical band. The observed adiabatic IP of this band is ~7.30 eV. The apparent band maximum at ~7.68 eV is mainly due to He Iβ ionization of the NO peak at 9.55 eV, and therefore the vertical IP of this band has not been determined. The adiabatic IP observed is close to that of 2-butyl radical, considering that the onset of a very low intensity band would be expected to yield a value which is too high.

Figure 4. He I spectrum of isobutyl radical and other pyrolysis products of 3-methyl-1-butyl nitrite. Peaks in the 9.2-10 eV spectral region arise from NO, propylene and methyl radicals. CH_2O is at 10.9 eV. Insert shows isobutyl radical band in greater detail. The weak band just before the isobutyl radical band is assigned to a secondary radical, possibly 2-butyl radical.

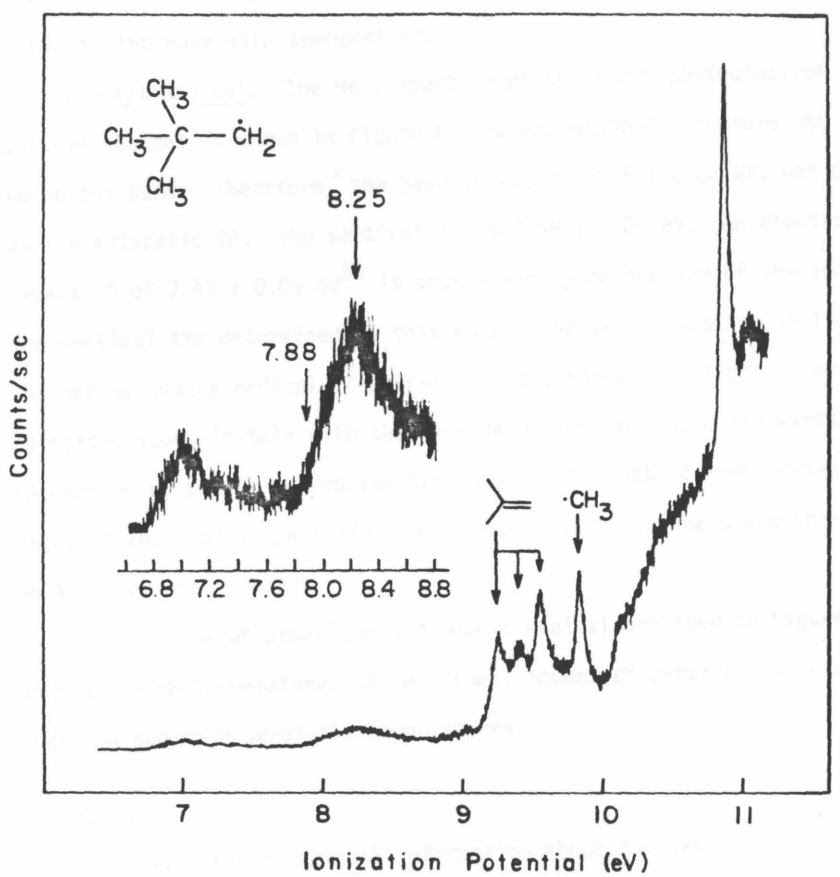

CH3
CH — ĊH2
CH3
8.31
7.93
7.2 7.6 8.0 8.4 8.8
·CH3
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

However, no definite assignment can be made. The isobutyl radical precursor sample was checked for purity and had no (<1%)[36] 2-butyl radical precursor. Over the 500 to 600 °C range, the ratio of the secondary radical band to the isobutyl radical band increases with temperature. Propylene, at 9.74 eV, and methyl radical, which coincides with the NO peak at 9.84 eV, are seen in Figure 4, and their production increases with temperature.

Neopentyl Radical. In Figure 5 is shown the He I spectrum of the first photoelectron band of neopentyl radical. A low pyrolysis temperature, 600 °C with the short pyrolyzer, was necessary to maximize the neopentyl radical spectrum. The adiabatic and vertical IPs are 7.88 ± 0.05 and 8.25 ± 0.03 eV, respectively. The adiabatic IP, chosen as the band onset, is in good agreement with an electron impact IP of 7.91 eV[29a]. No vibrational structure could be resolved on the band.

The photoelectron band that appears at lower ionization potentials is in the tertiary alkyl radical spectral region. The observed adiabatic and vertical IPs for this band are ~6.75 and ~6.98 eV, respectively, from the spectra taken at temperatures where the neopentyl radical band is a maximum. From a spectrum taken 50 °C higher, to maximize the tertiary radical band, a slowly rising onset at 6.68 eV was observed for this band. No definite spectral assignment can be made. The IPs are fairly close to those of tert-butyl radical (see Table I) and higher than would be expected for the tertiary C_5, 2-methyl-2-butyl, radical. By electron impact, the IP of 2-methyl-2-butyl radical is 0.08 eV lower than that of tert-butyl radical[29a]. Preliminary results indicate that the photoelectron spectrum of this radical, made directly from its nitrite precursor, has a slowly rising onset ~6.65 eV[29b]. No (<5%)[36] 2-methyl-2-butyl radical precursor was found in the neopentyl radical precursor sample. Over the 600 to 740 °C range, using the short pyrolyzer, the intensity of this tertiary radical band increases with

Figure 5. He I spectrum of neopentyl radical and other pyrolysis products of 3,3-dimethyl-1-butyl nitrite. Peaks in the 9.2-10 eV spectral region arise from NO, isobutylene and methyl radical. CH_2O is at 10.9 eV. Insert shows the neopentyl radical band in greater detail. The band at 7 eV is assigned to a tertiary radical, possibly 2-methyl-2-butyl radical.


CH3
CH3—C—ĊH2
CH3
8.25
7.88
6.8 7.2 7.6 8.0 8.4 8.8
·CH3
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

temperature, relative to the neopentyl radical band. The spectrum of isobutylene, a series of three peaks, the first and third of which are approximately coincident with the NO peaks at 9.26 and 9.55 eV[35,37], and the spectrum of methyl radical are observed in Figure 5. These pyrolysis products increase with temperature.

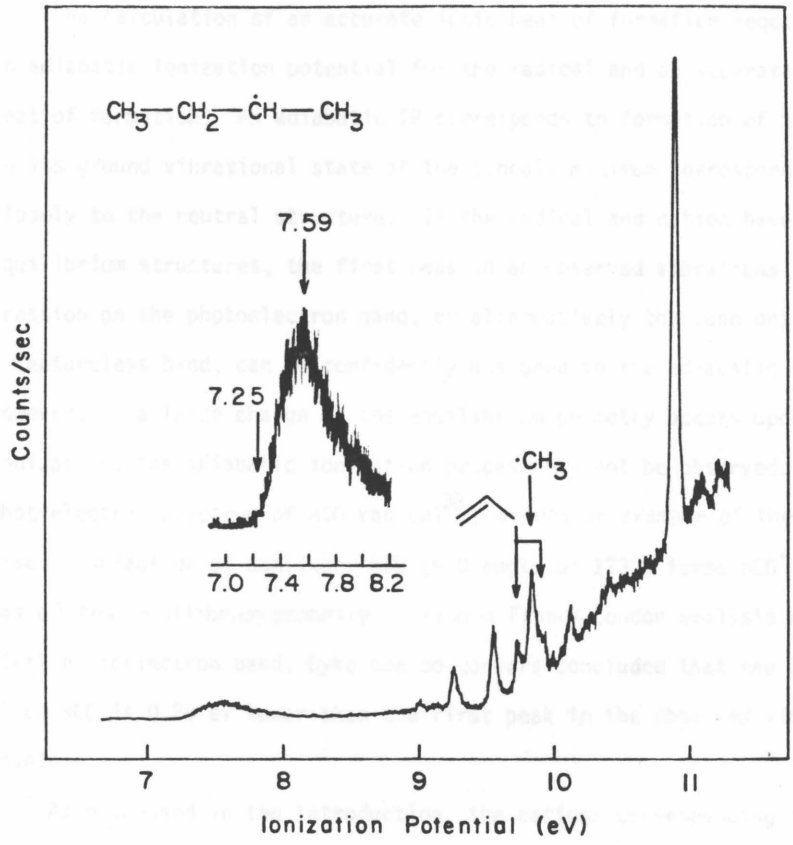
2-Butyl Radical. The He I spectrum of the first photoelectron of 2-butyl radical is shown in Figure 6. No vibrational structure was observed on the band. Therefore, the band onset, at 7.25 ± 0.02 eV, was chosen as the adiabatic IP. The vertical IP is 7.59 ± 0.03 eV. An electron impact IP of 7.41 ± 0.05 eV[18] is approximately an average of the adiabatic and vertical IPs determined in this work. The same situation is true for another secondary radical, 2-propyl radical, where the electron impact IP coincides approximately with the average of the adiabatic and vertical IPs determined by photoelectron spectroscopy[7]. In both of these cases the onset of the radical photoelectron spectrum is quite sharp and there is no evidence of hot bands.

The spectra of propylene and methyl radical are seen in Figure 6 and increase with temperature. A very small amount of 2-butene is observed at both low and high pyrolysis temperatures.

Discussion

To obtain thermochemical information about the cation, the ionization energetics from the photoelectron spectra must be combined with thermochemistry for the radicals. The photoelectron band shapes and resolved vibrational structure are indicative of the extent and type of geometry changes which the radical undergoes upon ionization. The photoelectron spectra are interpreted by analyzing them in conjunction with experimental and theoretical data pertaining to the structures of the radicals and the cations.

Figure 6. He I spectrum of 2-butyl radical and other pyrolysis products of 2-methyl-1-butyl nitrite. Peaks in the 9.2-10 eV spectral region arise from NO, propylene and methyl radical. CH_2O is at 10.9 eV. Insert shows the 2-butyl radical band in greater detail.


CH3—CH2—ĊH—CH3
7.59
7.25
·CH3
7.0 7.4 7.8 8.2
Counts/sec
7
8
9
10
11
Ionization Potential (eV)

Thermochemistry. Table II summarizes thermochemical data relating to the radicals and quantities derived for the ions from the photoelectron spectra of the radicals studied in this work. Similar data from earlier studies of other alkyl radicals are also included.

The calculation of an accurate ionic heat of formation requires an adiabatic ionization potential for the radical and an accurate radical heat of formation. An adiabatic IP corresponds to formation of the ion in its ground vibrational state at the (local) minimum corresponding most closely to the neutral structure. If the radical and cation have similar equilibrium structures, the first peak in an observed vibrational progression on the photoelectron band, or alternatively the band onset of a featureless band, can be confidently assigned to the adiabatic IP. However, if a large change in the equilibrium geometry occurs upon ionization, the adiabatic ionization process may not be observed. The photoelectron spectrum of HCO radical[38] provides an example of the later case. Ionization of nonlinear HCO (HCO angle of 123°) forms HCO^+ which has a linear equilibrium geometry. From a Franck-Condon analysis of the first photoelectron band, Dyke and co-workers concluded that the adiabatic IP of HCO is 0.28 eV lower than the first peak in the observed vibrational envelope.

As discussed in the Introduction, the cations corresponding to the primary radicals studied in this work may not be at local minima, and thus there may be no true adiabatic IPs corresponding to their formation. Instead, the true adiabatic IP would correspond to formation of the rearrangement product and may not be experimentally observable due to low Franck-Condon factors. Nevertheless, the photoelectron spectra could

Table II. Thermochemical Data for Radicals and Data for Cations Derived from Adiabatic Ionization Potentials Determined by Photoelectron Spectroscopy[a].

R	$\Delta H_f(R\cdot)$	$\Delta H_f(R+)$[b]	D(R - H)	$D(R^+ - H^-)$[b]	PA(Alkene)[b,c]	Alkene
CH_3	35.1[d] (35.1)[e]	262.0 (262.0)[e]	105.1	314.6		
CH_3CH_2	28.3[f] (25.9)	221.8 (219.4)	100.6	276.7	156.4	C_2H_4
2-C_3H_7	20.0[f] (18.2)	189.7 (187.9)	96.9	249.2	180.9	C_3H_6
t-C_4H_9	10.3[f] (8.7)	164.8 (163.2)	94.8	231.9	196.6	iso-C_4H_{10}
1-C_3H_7	22.6[g] (21.0)	210.5 (208.9)	99.5	270.0	160.1	C_3H_6
iso-C_4H_9	15.0[h] (13.4)[h]	197.9 (196.3)	99.5	265.0	163.5	iso-C_4H_{10}
neo-C_5H_{11}	7.1[h,i] (8.7)	188.8 (190.4)	99.5	263.8		
1-C_4H_9	17.0[h] (15.4)[h]	201.9 (200.3)	99.5	267.0	163.6	1-C_4H_{10}
2-C_4H_9	13.8[j] (13.0)	181.0 (180.2)	96.3	246.1	181.7	2-C_4H_{10}

[a]All quantities in kcal/mol at 298 K. Alkane and alkene heats of formation and the $\Delta H_f(H)$ from Ref. 46. Error limits ± 0.5 kcal/mol for methyl, ± 1.1 kcal/mol for ethyl, 2-propyl, 1-propyl and 2-butyl, ± 1.2 kcal/mol for tert-butyl, ± 2.3 kcal/mol for neopentyl and ± 3 kcal/mol for 1-butyl and isobutyl.

[b]All ionic heats of formation are calculated using the convention that the heat of formation of an electron at rest is zero at all temperatures. Therefore, $\Delta H_f(H^+)$ = 365.7 kcal/mol and $\Delta H_f(H^-)$ = 34.7 kcal/mol, Ref. 5b.

Table II. Continued

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[c]The proton affinity calculated is to form the given cation. This may not refer to protonation at the most probable site in the alkene.

[d]Ref. 42.

[e]Quantities in parenthesis are the radical heats of formation from Ref. 42 and the corresponding cation heats of formation derived from the photoelectron data.

[f]Designated "1981 values," Ref. 41.

[g]Ref. 43.

[h]Calculated assuming $D(R - H) \cong D(1\text{-}C_3H_7\text{-}H) \pm 2$ kcal/mol.

[i]Essentially the same value for ΔH_f (neo-C_5H_{11}) is obtained using an experimental determination of $D(\text{neo-}C_5H_{11}\text{-}H) = 99.3 \pm 1$ kcal/mol, Ref. 47a. In reasonable agreement with a 4.0 ± 1 kcal/mol difference between D(R - H) for methane and neopentane, Ref. 47b.

be used to calculate useful thermochemical quantities because the observed photoionization processes are indeed limited by the accessible Franck-Condon region.

To calculate the heat of formation of the cation with a structure closest to that of the radical, the vertical ionization potential would be used. Even in those cases where the corresponding cation is at a potential energy minimum, the equilibrium cation geometry is somewhat different from the radical geometry. This is reflected in the photoelectron spectra of alkyl radicals, such as 2-propyl and tert-butyl radicals, since adiabatic and vertical IPs do not coincide[7]. To calculate heats of formation of the primary cations in a manner consistent with those calculated for known stable cations by allowing them to reflect stabilization achieved by the cation by small deviations from the radical geometry, the lowest energy ionization observed in the radical photoelectron spectrum has been used. If the cation is at a local minimum, this quantity should be the true adiabatic IP. In the absence of a local minimum corresponding to the cation, it represents a somewhat vague limit. With these qualifications in mind, the apparent adiabatic IP of 1-propyl radical, for example, is associated with formation of 1-propyl cation. It is noted that the heat of formation of 1-$C_3H_7^+$ in Table II is much higher than that of 2-$C_3H_7^+$ calculated using the adiabatic IP of 2-propyl radical.

The other quantity needed to calculate an accurate cation heat of formation from the photoelectron data is a heat of formation for the radical. Recently, the accuracy of the widely accepted Benson values[39] for the heats of formation of alkyl radicals, other than methyl radical,

has been questioned. Many experiments by other workers have suggested that the heats of formation should be revised upward[40,41]. The most recent review on the subject[42], however, after examining the conflicting evidence concerning the heat of formation of tert-butyl radical which is at the center of the controversy, adopted a slightly updated version of the previously well-accepted lower values for alkyl radical heats of formation.

In this work, the somewhat higher radical heats of formation are used. Employing the heats of formation of 1-propyl[43] and 2-butyl[44] radicals from recent determinations and the heats of formation of 1-butyl, isobutyl and neopentyl radicals, calculated assuming D(R-H) is approximately equal to D(1-C_3H_7-H), the heats of formation of the corresponding ions were calculated. Thermochemical data derived from photoelectron data[7] on other alkyl radicals were calculated also using recently determined values for the radical heats of formation (the designated "1981 values" of Doering[41,45]). The thermochemistry of the methyl, ethyl, 2-propyl and tert-butyl cations listed in Table II is somewhat different from previously cited[7] values determined from the photoelectron spectra of the radicals because slightly higher radical heats of formation have been used.

For comparison, the previously well-accepted lower radical heats of formation and the resulting cation heats of formation derived from the photoelectron data are listed in parentheses in Table II. These values will not be used in subsequent discussion. However, it is noted that the relative cation heats of formation differ only slightly between the two sets. Since the large majority of the comparisons between the photoelectron data and other experimental or theoretical studies involve relative cation heats of formation, not absolute values, the conclusions

are nearly independent of the set of radical heats of formation used.

Combining the heats of formation of the ion with known alkane and alkene heats of formation, the hydride affinity of the ion ($D(R^+-H^-)$) and the proton affinity (PA) of the corresponding alkene can be determined and are listed in Table II. It has been noted that typical primary, secondary and tertiary ions have characteristic hydride affinities and that the hydride affinities can be used to evaluate the relative stabilities of ions[29,48]. Referring to the data in Table II, all the primary ions have similar hydride affinities. Furthermore, β- and, to a lesser extent, γ-methyl substitution in a primary ion decreases the hydride affinity, indicating an increased stability of the ion. Similarly, 2-butyl cation has a hydride affinity somewhat below that of 2-propyl cation.

Thresholds for formation of fragment ions from hydrocarbons often correspond to formation of the most stable isomer, even when extensive rearrangements are required[49]. Exceptions are known, however. For example, photoionization appearance potentials at 300 K for CH_3 ($\Delta H_{f\,298}(CH_3)$ = 35.1 kcal/mol[39]) loss from n- and isopentane[50] give $\Delta H_{f\,298}(C_4H_9^+)$ = 182.3 ± 1.0 and 181.0 ± 1.0 kcal/mol, respectively, both of which apparently correspond to $2\text{-}C_4H_9^+$ and not to tert-$C_4H_9^+$. These values are in very close agreement with the $\Delta H_{f\,298}(2\text{-}C_4H_9^+)$ of 181.0 ± 1.1 kcal/mol determined here. The ionic heats of formation derived above were calculated assuming the appearance potential (AP) measured at 298 K is the energy to form the products of the fragmentation process at 298 K from reactants at 298 K. A recent photoionization study[51] assumed that the AP measured at 298 K corresponds to products formed at threshold with 0 K translational energy and essentially 0 K

internal energy from reactants at 298 K. Based on this assumption, a slightly higher heat of formation at 298 K for 2-butyl cation of 184.3 ± 0.7 kcal/mol was calculated using AP measurements of $C_4H_9^+$ from 2-substituted butanes[52]. The 3.3 ± 1.4 kcal/mol discrepancy between the photoelectron and these photoionization results may be due to an adiabatic AP which is too low in intensity to observe, an adiabatic IP which was chosen too low, or a radical heat of formation which is too low. Ideally the adiabatic IP is chosen as the maximum of the first peak in a resolved vibrational progression, and this should correspond approximately to the Q band of the 0,0 ← 0,0 transition energy[7]. For the 2-propyl and tert-butyl radical photoelectron spectra, the adiabatic ionization potentials, which were chosen as the maximum of the first vibrational peak, are approximately 0.03 - 0.04 eV higher than the band onset. By comparison, we would expect that the adiabatic IP for 2-butyl radical, which was chosen as the band onset, could be too low by no more than 1 kcal/mol. Since the pyrolysis temperature is low and the band onset is sharp, it seems unlikely that hot bands contribute to the spectrum.

From equilibrium constants for proton-transfer reactions measured in the high-pressure ion source of a mass spectrometer, the heat of formation of 2-$C_4H_9^+$ is calculated to be 183.2 ± 2.2 kcal/mol, relative to a heat of formation for 2-$C_3H_7^+$ of 191.7 ± 2.1 kcal/mol (a difference of 8.5 kcal/mol)[53]. From rate constants of proton-transfer reactions observed in a pulsed ion cyclotron resonance spectrometer, the heat of formation of 2-$C_4H_9^+$, relative to that of tert-$C_4H_9^+$, was found to be +14.6 ± 1.4 kcal/mol[54]. From the photoelectron results presented in Table II, the heat of formation of 2-$C_4H_9^+$ relative to 2-$C_3H_7^+$ is -8.7 ± 1.6 kcal/mol, and relative to tert-$C_4H_9^+$ is +12.0 ± 1.7 kcal/mol, in good agreement with the

proton-transfer results.

Solution-phase data on the relative heats of formation of cations can be compared to the gas-phase results. The difference between the heats of formation of 2-butyl and tert-butyl cations, in a SO_2ClF/SbF_5 solution, has been measured by calorimetry to be 14.3 ± 0.5 kcal/mol[4b]. Our gas-phase determination of this energy difference is 16.2 ± 1.6 kcal/mol. These agree within the uncertainties in the measurements, supporting previous conclusions that differential solvation energetics of isomeric cations are small[2a,4b,55].

The difference between the heats of formation of 1-propyl and 2-propyl cations is 20.8 ± 1.6 kcal/mol as determined from the photoelectron data. This is somewhat larger than a previous value of 16 kcal/mol calculated from IPs for the radicals determined by electron impact[18]. The third $C_3H_7^+$ isomer, protonated cyclopropane, is probably intermediate between the two, but its heat of formation is not well known[56]. This difference of 20.8 kcal/mol can be compared to a recent estimate of 16.4 ± 0.4 kcal/mol for the energy of activation for proton exchange in 2-propyl cation in SO_2ClF/SbF_5 solution[19,57]. This was derived from NMR lineshape analysis over the 0° to 40°C temperature range. One mechanism proposed for the exchange involves isomerization of 2-propyl to 1-propyl cation followed by closure to a protonated cyclopropane (which is necessary to account for ^{13}C scrambling). Formation of 1-propyl cation is likely to be the most endothermic step. Therefore, the 16.4 kcal/mol activation energy can be taken to be a measure of the difference in energy of the two isomers in solution plus the activation energy for the reverse reaction, assumed to be very small in the case of a primary to secondary cation rearrangement[57]. If this mechanism is correct, then it would

appear that solvent participation in the isomerization must be important. Another explanation is that the primary cation is not an intermediate. The other mechanism proposed[57] involves a concerted rearrangement involving only 2-propyl cation and protonated cyclopropane. The activation energy may then reflect the energy difference between these two structures.

The NMR spectrum of 2-butyl cation[22] indicates that scrambling of all the protons occurs over the -110° to -40° C temperature range, compared to 0° to 40° C for 2-propyl cation[57]. Since the barrier for this process must be much lower than for the equivalent process in 2-propyl cation, a primary cation intermediate was considered to be unlikely. This conclusion is confirmed by our results since the differences between 1- and 2-propyl cation and 1- and 2-butyl cation are both ~20 kcal/mol. Assuming a protonated methylcyclopropane intermediate, Saunders et al.[22] calculated an E_a of 7.5 ± 0.1 kcal/mol for complete proton scrambling in 2-butyl cation. At higher temperatures, 2-butyl cation converts to tert-butyl cation. From the rate observed at -41° C and assuming a normal log A, the barrier to this reaction is estimated to be 18 kcal/mol[22]. Isobutyl cation was suggested as a possible high-energy transition state for the reaction so that 18 kcal/mol could represent the energy difference between 2-butyl and isobutyl cations. An alternative mechanism proposed involves cyclization of 2-butyl cation to a protonated methylcyclopropane and then a concerted rearrangement through a high-energy transition state to give tert-butyl cation without an isobutyl cation intermediate. The gas-phase energy difference between 2-butyl and isobutyl cation isomers, 16.9 ± 3 kcal/mol from the photoelectron results, is consistent with the intermediacy of isobutyl cation.

A closer examination of these comparisons may be used to support an expected, albeit weak, trend in solvation energetics. The gas-phase difference in the heats of formation of 2-butyl and tert-butyl cations is 1.9 kcal/mol larger than the solution-phase value. Assuming 1-propyl cation is an intermediate in the rearrangement of 2-propyl cation, the gas-phase difference in their heats of formation is 4.4 kcal/mol larger than the value in solution. Disregarding the comparison with the energetics for rearrangement of 2-butyl to tert-butyl cation in solution, which is only an approximate value, the two differences listed above suggest that solvation energies decrease in the order primary ion > secondary ion > tertiary ion. This trend can be explained by the Born model of ionic solvation. In a tertiary ion the charge is expected to be more delocalized, extending over a larger region, than in a primary ion and thus the tertiary ion is more poorly solvated.

Radical and Cation Structures. The first photoelectron bands of the primary and secondary alkyl radicals studied in this work are fairly broad and, with the exception of 1-propyl radical, exhibit no resolved vibrational structure. This is indicative of significant geometry change on ionization, which has been found for other acyclic alkyl radicals larger than methyl radical[7].

ESR and IR spectroscopy and theoretical calculations of the radicals yield a fairly detailed picture of the radical structures. Matrix isolation studies of infrared spectra[58-60] of primary and secondary radicals have shown that CH stretching frequencies associated with the radical centers are typical of centers having sp^2 hydridization. From this it is inferred that primary and secondary radical centers are nearly

planar. Geometry-optimized ab initio calculations give out-of-plane angles of 9-11° for 1-propyl[61], isobutyl and neopentyl radicals[62]. Effects of the unpaired electron on bonds beta to the radical center have been observed. Infrared spectroscopy indicates that the β C-H bonds in alkyl radicals are long and weakened compared to alkane C-H bonds[58]. This is consistent with the lengthening of bonds beta and eclipsed to the radical center observed in theoretical calculations[61,62]. These calculations also indicate that the C_α-C_β bond is somewhat shorter than a normal C-C single bond length.

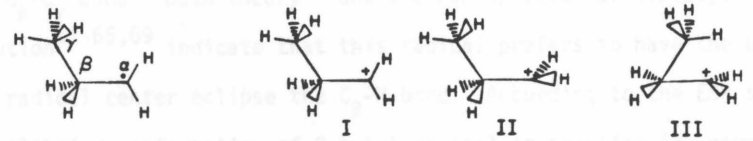
ESR spectra of radicals have been interpreted in terms of preferred radical conformations and barriers to rotation about the C_α-C_β bond. Results of analyzing many alkyl radical ESR spectra suggest that the equilibrium conformations in alkyl radicals are determined by a delicate balance between steric repulsions and the optimization of β C-H hyperconjugation with the singly occupied p orbital on the radical center[63]. The conformational preferences appear to be weak, however[63]. For example, the rotational barriers about the C_α-C_β bond in 1-propyl and isobutyl radicals estimated from their ESR spectra are very low ($\leq$0.5 kcal/mol)[63,65,69]. Theory is in agreement with this picture[61,62].

The structure of 1-propyl radical has been the most extensively studied by both theory and experiments[58,59,61,63-69]. It has been deduced from ESR data that the preferred conformation of the radical in solution has one of the C_α-H bonds eclipsing the C_β-C_γ bond (see Figure 7)[63-65]. Two studies[66,67] at 4 K in solid argon matrices have suggested, however, that the H_α-C-H_α plane actually oscillates between two minima located 10°[66b] or 30°[67] on either side of the C_β-C_γ bond. Theoretical calculations indicate both possibilities to be very close in energy[61,68].

The preferred conformations of the other radicals are also shown in

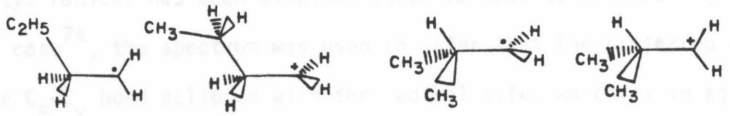
Figure 7. Preferred radical conformations inferred from ESR spectra and cation conformations taken from theoretical calculations.

1-PROPYL



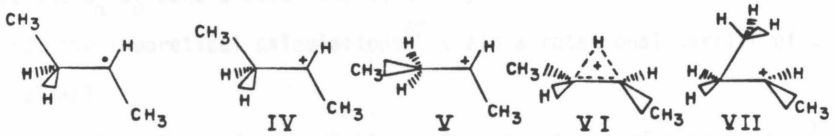
Radical Cation

1-BUTYL ISOBUTYL



Radical Cation Radical Cation

2-BUTYL



Radical Cation

Figure 7. The ESR spectrum of 1-butyl radical in solution indicates that the preferred conformation of the radical is analogous to that of 1-propyl radical. One of the C_α-H bonds is eclipsing the C_β-C_γ bond[69-71]. Similarly, studies of 1-butyl radical in argon matrices have suggested that the H_α-C-H_α plane oscillates between two minima located 23°[66b] or 30°[67] on either side of the C_β-C_γ bond. Both theory[62] and the ESR spectrum of isobutyl radical in solution[63-65,69] indicate that this radical prefers to have the p orbital on the radical center eclipse the C_β-H bond. According to the ESR spectrum, the equilibrium conformation of 2-butyl radical in solution is unsymmetrical, analogous to that for 1-propyl radical in solution[64,69,72]. Presumably, the methyl groups on the α and β carbons are anti[72]. The ESR spectrum of neopentyl radical has been obtained under various conditions[64,73-76]. In one case[74], the spectrum was used to infer that the preferred conformation has one C_β-C_γ bond eclipsed with the radical site, which is in agreement with the theoretical results[62]. The conformational preference would be expected to be very weak since the totally symmetric six-fold rotation about the C_α-C_β bond should lead to a very small rotational barrier[76,77]. Indeed, the theoretical calculations[62] yield a rotational barrier of only 160 cal/mol.

The only information available on the structures of primary ions comes from theory. The $C_3H_7^+$ potential energy surface has been the most well studied by ab initio[8,9,78,79] and semiempirical methods[9,10]. Under the constraint of maintaining C_s symmetry, three local minima were found for 1-propyl cation using ab initio techniques and an STO-3G basis set[78]. Although higher-level calculations[8,79] reveal that these geometries are not local minima, their energies and structures provide useful information about the $C_3H_7^+$ potential energy surface in the region of the radical structure. As shown in Figure 7, these three local minima correspond

to a conformation very similar to that of the radical (I), a conformation similar to the first except that the C_α-H bonds are staggered with respect to the C_β-C_γ bond (II), and a structure resembling that of a distorted corner-protonated cyclopropane (III). The cation centers are planar or nearly so. For example, structure II has an out-of-plane angle of 5° with the hydrogens bent toward the terminal methyl group. All three geometries have C_α-C_β bonds which are shorter than C-C bonds in propane. In structures II and III, where the empty p orbital is eclipsing the C_β-C_γ bond, the C_α-C_β bond is shorter than the C_α-C_β bond length calculated for 1-propyl radical[61]. This preference for optimizing the interaction between the empty p orbital and the C_β-C_γ bond is also reflected in the relative energies of these structures. The most detailed calculation of their energies, including polarization functions at the 6-31G* level, determined that structure III is more stable than I by 4.7 kcal/mol and I is 1.8 kcal/mol higher in energy than II[79]. Another calculation, which included electron correlation effects, also found that I is higher in energy than II, in this case by 2.0 kcal/mol[9]. This energy difference is assigned to the rotational barrier about the C_α-C_β bond in II[78,79]. Thus, in the absence of symmetry constraints, I is not at a local minimum. On the basis of the relative energies of various $C_3H_7^+$ structures calculated at the 6-31G* level, it is concluded that III can be considered as a distortion of corner-protonated cyclopropane and not a local minimum. Geometry optimization at the 6-31G* level reveals that 1-propyl cation (II) is not a local minimum on the potential energy surface[8]. MINDO/3 semiempirical calculations are in agreement with these results[9,10]. Both methods found that 1-propyl cation is converted without activation to protonated cyclo-

propane[8,10]. An energy for 1-propyl cation was obtained at the 6-31G* level by imposing a symmetry constraint, a C_s plane, and calculating the energy of the optimized structure I. Including electron correlation effects, 1-propyl cation (I) is 19.7 kcal/mol less stable than 2-propyl cation[8]. MINDO/3 calculations yield values of 18.6[10] and 18.87[9] kcal/mol for the energy difference between 1-propyl and 2-propyl cations. These theoretical values are in good agreement with the experimental difference in energy between 1-propyl and 2-propyl cations, 20.8 ± 1.6 kcal/mol, determined from the photoelectron data. The ab initio value is in closest agreement, although it would have been expected that this value be somewhat larger than the experimental since II is predicted to be the more stable 1-propyl structure. Given the essentially free rotation about the C_α-C_β bond in the radical, the adiabatic IP of 1-propyl radical should most closely correspond to formation of 1-propyl cation (II).

Although theory has not studied in detail the $C_4H_9^+$ and $C_5H_{11}^+$ potential energy surfaces, ab initio techniques have been used to determine the most stable conformations of the radical-like, or classical, structures of the cations. Using a set of fixed standard geometries appropriate for classical carbonium ions and a STO-3G basis set, the energy of the eclipsed and perpendicular conformations (I and II, repsectively, for 1-propyl cation) of 1-propyl, 1-butyl, isobutyl, neopentyl and 2-butyl cations have been calculated[80]. The results indicate that the preferred conformation of the cation is determined largely by the relative hyperconjugative abilities of the bonds at the beta carbon. C-C hyperconjugation is found to be much more effective than C-H hyperconjugation. This is in contrast to the weak preference for C-H hyperconjugation displayed

by the radicals. The stronger conformation preferences displayed by primary cations compared to primary radicals has been noted previously[81]. The preferred conformations are shown in Figure 7. 1-Propyl cation prefers the perpendicular (II) over the eclipsed conformation by 2.5 kcal/mol at this level of calculation. Similarly, 1-butyl cation prefers the perpendicular conformation by 3.7 kcal/mol. To maximize C-C hyperconjugation, isobutyl cation prefers the eclipsed conformation by 2.7 kcal/mol. For neopentyl cation, neither conformation is preferred and so there is no barrier to rotation about the C_α-C_β bond, which is to be expected by symmetry. The perpendicular conformation of 2-butyl cation (V) is preferred over the eclipsed conformation (IV) by 2.2 kcal/mol.

The relative energies of the classical $C_4H_9^+$ species were also determined at the STO-3G level. 1-Butyl, isobutyl, and 2-butyl cations are 37, 37, and 17 kcal/mol, respectively, higher than tert-butyl cation according to these calculations[80]. This is in reasonable agreement with the corresponding values of 37.1, 33.1 and 16.2 kcal/mol determined from the photoelectron data in Table II. The good agreement between the relative energies calculated for the classical structures of the $C_3H_7^+$ and $C_4H_9^+$ ions and the energies determined from the photoelectron data is consistent with the notion that the apparent adiabatic IPs of the radicals studied in this work correspond to formation of cations with structures similar to those of the radicals.

Even when the same bonding configuration is retained, the theoretical and experimental studies discussed above indicate that in going from the radical to the cation the preferred bond lengths, bond angles and rotational conformations change. These geometry changes explain why the vertical and adiabatic IPs of the radicals do not coincide and should also offer

possible explanations for the origin of the 540 ± 160 cm^{-1} vibration progression resolved on the 1-propyl radical photoelectron band. Those vibrations which correspond most closely to the change in equilibrium geometry occurring upon ionization will be most strongly excited. Since in going from the radical to the cation, the configuration at C_α is expected to become more planar and the C_α-C_β bond is expected to shorten to enhance C-C hyperconjugation with the cation center, it is likely that out-of-plane bending and skeletal stretching modes are excited. Both tert-butyl and 2-propyl radicals undergo excitation of analogous vibrations on ionization, as evidenced from assigned resolved vibrational progressions on their photoelectron bands[7]. The corresponding frequencies for these modes in 1-propyl cation would both be approximately 1000 cm^{-1}, too high in energy to correspond to the 540 cm^{-1} mode observed and hence are probably not resolved. Another major difference between the radical and ion structures is the conformational preference of the CH_2 group. Thus, excitation of torsions about the C_α-C_β bond would be expected, but would probably involve a frequency much lower than 540 cm^{-1}. Finally, it is possible that the Franck-Condon region includes part of the reaction coordinates leading to isomerization of 1-propyl cation to 2-propyl cation (1,2-hydride shift) or a protonated cyclopropane (C-C-C bending motion). Excitation of modes leading to motion along the reaction coordinate might be observed.

The fact that the photoelectron spectra of the other primary radicals presented here do not have resolved vibrational structure is not very surprising. The vibrational structure on the photoelectron band of 1-propyl radical is weak and, with larger radicals, more torsional and

vibrational modes may be excited upon ionization. The overlapping of several vibrational progressions can result in a featureless band. Although the spectrum of 2-propyl radical clearly reveals vibrational structure, the larger 2-butyl radical may also have a featureless band due to more vibrational modes being excited upon ionization. This is particularly likely given the stronger interaction of the cation center with the added β methyl than with the β hydrogens, which was indicated by the theoretical calculations. The absence of structure may also be an indication that the ion is not stable with respect to isomerization. This would result in excitation of very closely spaced vibrational levels, which in turn would tend to mask structure that would otherwise be observable. Therefore, the presence of structure on the 1-propyl radical spectrum suggests that 1-propyl cation may be at a local minimum on the $C_3H_7^+$ potential energy surface. If 1-propyl cation is formed in an energy minimum, the failure to observe unrearranged 1-propyl cation experimentally in the gas phase[1a,1b,11,14,15] implies there is a low barrier to isomerization.

The general shape of the first photoelectron band also contains information regarding the ionic potential energy surface relative to the ground state radical potential energy surface. The view of the ionic potential energy surface reflected in the photoelectron band is expected to be limited, by the Franck-Condon factors, to the region of the cation species with a geometry not very different from that of the radical. Assuming the band shape reflects the overlap of vibrational wavefunctions of the classical cation with those of the radical, a simple interpretation can be made. Radom, Pople and Schleyer[80] concluded that the preferred

classical cation geometry is that which maximizes C_β-C_γ hyperconjugation with the empty p orbital on the ion center. The inductive and hyperconjugative contributions to the β-methyl stabilizing effect on alkyl cations were studied by assuming the former is conformationally independent and the later conformationally dependent[77]. By considering structurally independent and dependent effects, the photoelectron spectra of the corresponding radicals can offer an experimental verification of these contributions.

Both vertical and adiabatic IPs of alkyl radicals generally decrease with increased substitution at the beta carbon. The vertical IP is determined by that vibrational wavefunction in the ion which has the largest amplitude at the equilibrium geometry of the radical. Trends in vertical IPs should reflect trends in the inductive stabilization offered by the substituents since to optimize the hyperconjugation stabilization available, the cation must adopt a geometry different from that of the radical, in particular a shorter C_α- C_β bond. Reflecting the increasing inductive stabilization with β-methyl substitution, the vertical IPs in the series ethyl, 1-propyl, isobutyl and neopentyl radicals are 8.51, 8.43, 8.31 and 8.25 eV, respectively, and in the series 2-propyl and 2-butyl radicals are 7.69 and 7.59 eV, respectively. The vertical IP of 1-butyl radical (8.50 eV) is higher than than of 1-propyl radical (8.43 eV). There is no obvious explanation for this since the terminal methyl group in 1-butyl cation would not be expected to destabilize the radical-like conformation.

The difference between the adiabatic and vertical IPs is that amount of extra stabilization available when the ion is allowed small

conformational deviations from the radical equilibrium geometry and thus should reflect the hyperconjugative stabilization available. This difference is 0.12, 0.28, 0.38, and 0.37 eV for the series ethyl, 1-propyl, isobutyl and neopentyl radicals, respectively. The first two methyl substituents on the β carbon result in successive "broadening" of the photoelectron band. The last methyl group appears to have no additional hyperconjugative effect since the isobutyl and neopentyl radical bands are equally "broad." This is not surprising, since hyperconjugative stabilization is expected to be a function of the dihedral angle between the empty p orbital and the C_β-C_γ bond[80]. The maximum hyperconjugative stabilization available from each C_β-C_γ bond in neopentyl cation is not simultaneously achieved. Steric effects may also decrease the stabilization available per methyl group. The difference between the adiabatic and vertical IPs for 1-propyl and 1-butyl radicals is 0.28 and 0.48 eV, respectively, and for 2-propyl and 2-butyl radicals is 0.33 and 0.34 eV, respectively. Steric interactions may have some effect since it is somewhat surprising that the difference between the adiabatic and vertical IPs of 2-butyl radical is essentially the same as that of 2-propyl radical.

Radom, Pople and Schleyer[80] concluded that for primary cations the inductive and hyperconjugative effects of the alkyl group beta to the cation center make approximately equal contributions on the order of several kcal/mol and that they follow the normal inductive order: $t\text{-}C_4H_9 > 2\text{-}C_3H_7 > C_2H_5 > CH_3$. Our results are in general agreement with these findings.

NMR spectroscopy has been used extensively to study the low-energy conformations of 2-butyl cation [23,25,82]. An empirical additive substituent effect method for estimating ^{13}C NMR shifts was applied to

the 2-butyl cation spectrum[24]. It was concluded that 2-butyl cation in SbF_5/SO_2ClF solution at low temperatures (-80 to -130° C) is best represented as equilibrating between a classical secondary cation (structures IV and V, Figure 7) and a hydrogen-bridged species (VI) of very similar energy. From the absence of line broadening in the ^{13}C NMR spectrum of 2-butyl cation in solution at -140° C, an upper limit of 2.4 kcal/mol for $\Delta G^{\ddagger}$ was determined for the degenerate 1,2 hydride shift[82]. Even in the solid state at -190° C, there is no evidence for a static 2-butyl cation[23]. Recently, Saunders and coworkers studied the effect of isotopic perturbation[83] on the NMR spectrum of 2-butyl cations. Their interpretation of the results indicates that the secondary cation structure is at a local minimum 0.4 kcal/mol above the more stable hydrogen-bridged species, with a barrier of less than 2 kcal/mol for rearrangement of the hydrogen-bridged species to the classical cation[25].

The heat of formation of 2-butyl cation determined in this work is in close agreement with proton-transfer[53,54] and several appearance potential measurements[50], as discussed previously. This is consistent with the NMR results. Since Franck-Condon factors for ionization to a hydrogen-bridged species would be expected to be small, the adiabatic IP probably corresponds to formation of the radical-like cation structure. If there is a low barrier to rearrangement to a more stable structure, the other techniques would be expected to measure the heat of formation of this structure. A 0.4 kcal/mol difference between the photoelectron results and the others, as suggested by the NMR experiments, could not be detected. The appearance potential measurements[52] which are only in fair agreement with the photoelectron results yield a heat of formation of 2-butyl cation

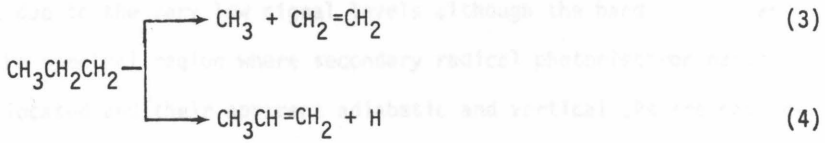
which is higher, and thus the discrepancy cannot be explained using this argument. Using structures optimized at the STO-3G and the MINDO/3 level, ab initio calculations including electron correlation effects and estimating the effect of polarization functions indicate that the hydrogen-bridged 2-butyl structure (VI) is 8-10 kcal/mol lower than the classical structure[84]. At a similar level of theory, the hydrogen-bridged structure of ethyl cation is 8 kcal/mol lower than the classical[85]. There is evidence that the most stable ethyl cation structure is significantly different from that of ethyl radical. Heats of formation of ethyl cation determined from photoionization appearance energies, 216.0 ± 0.5[51] and 215.3 ± 1.0[86] kcal/mol, predict an adiabatic IP of ethyl radical of 8.12 ± 0.08 eV, well below the value of 8.39 ± 0.02 eV[7] determined by photoelectron spectroscopy and below the photoelectron band onset at ~8.32 eV. The difference between the predicted and apparent adiabatic IPs suggests that hydrogen-bridged ethyl cation is 6 ± 2 kcal/mol lower in energy than the classical structure, in agreement with theory. Either the theory overestimates the stability of the hydrogen-bridge 2-butyl cation and the NMR results in stable-ion media are a better reflection of the energy differences in the gas phase, or the thermochemistry of the $C_4H_9^+$ system is not sufficiently well determined to detect the energy difference, or there is a large barrier for the rearrangement.

Using fixed geometries based on optimized structures of 1-propyl and 2-propyl cations, ab initio calculations at the 4-31G level found another low-energy 2-butyl cation structure. A partially methyl-bridged structure (VII) is calculated to be 15 kcal/mol more stable than 2-butyl cation (V), although a fully bridged structure, corner-protonated methylcyclopropane,

is only 0.6 kcal/mol more stable than V. The NMR experiments on 2-butyl cation[22] reveal no evidence for such a stabilized structure but instead are consistent with a protonated methylcyclopropane species being 2-7 kcal/mol higher in energy than 2-butyl cation. Gas-phase experiments indicate that protonated methylcyclopropane is also higher in energy than 2-butyl cation, by ~10 kcal/mol[53]. The calculations may overestimate greatly the stability of the partially methyl-bridged structure.

Thermal Decomposition of Radicals. As shown in the Experimental Section, the direct products of the thermal decomposition of the nitrite precursor are observed in the photoelectron spectra as well as other species, which can be ascribed to subsequent decomposition reactions of the initial radicals formed[88,26]. Overlapping photoelectron spectra may obscure some products and, unless a spectrum is sharp or otherwise characteristic, a positive assignment may be difficult. Only those intermediates which can survive ~1 msec in the heated region will be detected in the photoionization region.

The following reactions can account for most of the products observed in the pyrolysis spectra:



(3)

(4)

$$CH_3CH_2CH_2CH_2 \longrightarrow CH_3CH_2 + CH_2{=}CH_2 \qquad (5)$$

$$(CH_3)_2CHCH_2 \longrightarrow CH_3 + CH_3CH{=}CH_2 \qquad (6)$$

$$(CH_3)_3CCH_2 \rightarrow CH_3 + (CH_3)_2CH{=}CH_2 \qquad (7)$$

$$CH_3CH_2CHCH_3 \rightarrow CH_3 + CH_2{=}CHCH_3 \qquad (8)$$

$$CH_3CH_2CHCH_3 \rightarrow CH_3CH{=}CHCH_3 + H \qquad (9)$$

Surface reactions may be responsible for the small amount of H atom loss products (reactions 4 and 9) since they are observed at low temperatures and their yield does not appear to increase at higher temperatures. Based on their Arrhenius parameters, the reaction involving C-C bond cleavage in 1-propyl radical is much faster than homogeneous H atom loss[89]. This conclusion also applies to 2-butyl radical. Homogenous H atom loss competes so unfavorably with C-C bond cleavage that its rate has not been measured[90]. H atom loss products for 1-butyl and isobutyl radical, 1-butene and isobutylene, respectively, could not be detected. The C-C bond cleavage reactions observed in this study (3, 5, 6, 7, and 8) have all been reported to be the major decomposition pathways for the respective radicals[89].

In the studies of 1-butyl and isobutyl radicals, very low intensity photoelectron bands appeared near the onset of the photoelectron spectra assigned to these primary radicals. No positive assignment could be made due to the very low signal levels although the bands do appear in the spectral region where secondary radical photoelectron bands are located, and their apparent adiabatic and vertical IPs are not inconsistent with the spectrum of 2-butyl radical. In the neopentyl radical pyrolysis spectrum, significant amounts of a tertiary radical appeared whose spectrum is close to that of tert-butyl radical and could be due to the C_5 tertiary radical. An explanation consistent with these observations is the occurrence of radical isomerizations (reactions 10-12)

under the conditions of our experiments.

$$CH_3CH_2CH_2CH_2 \rightarrow CH_3CHCH_2CH_3 \quad (10)$$

$$(CH_3)_2CHCH_2 \rightarrow CH_3CHCH_2CH_3 \quad (11)$$

$$(CH_3)_3CCH_2 \rightarrow (CH_3)_2CCH_2CH_3 \quad (12)$$

In a study of isomeric C_4H_7 radicals by photoelectron spectroscopy[91], several radical rearrangements are observed which have been previously noted under other experimental conditions. There is some evidence that reaction 10 has been observed before[89] by the detection of propylene, a product of 2-butyl radical decomposition, from thermolysis of 1-butyl radical[92]. A small peak which may be assigned to propylene was observed in photoelectron spectra of the pyrolysis products of the 1-butyl radical precursor. However, reactions 11 and 12 appear never to have been observed, nor investigated, previously. Reaction 10 can be interpreted as a 1,3 or 1,2 H atom shift, both of which occur for vibrationally excited pentyl radicals with estimated activation energies of ~31 and ~33 kcal/mol, respectively[93]. Similar activation energies have been measured for the β C-C bond-breaking processes, reactions 3, 5, 6, 7, and 8. The Arrhenius factor for the rearrangement would be expected to be significantly lower than that for a simple bond-breaking process. Reactions 11 and 12 can be explained by 1,2 CH_3 shifts. The rearrangment of neopentyl radical appears to be much more facile than that of isobutyl radical, perhaps reflecting a larger statistical factor and/or a preference for formation of a tertiary radical over a secondary radical product. Theory[94] has indicated that 1,2 CH_3 shifts, like 1,2 H shifts, are high-energy processes. It is often suggested that the lowest energy pathway for formation of such products involves

elimination and readdition of the methyl group[95]. The low-pressure conditions of our experiments make the later route very unlikely. However, the radicals experience several collisions with the pyrolyzer wall. All three of these rearrangements could take place via heterogeneous wall-catalyzed mechanisms. Since the activation energies for the truly unimolecular rearrangement and for the decomposition may be very close, the rearrangement products would have enough energy to decompose rapidly and thus would not be detected. A heterogeneous rearrangement mechanism may offer a means by which less activated products would be formed.

Admittedly, these suggested mechanisms are somewhat speculative since no definite spectral assignments could be made except to identify the products as secondary or tertiary alkyl radicals. Hydrogen atom abstraction from the nitrite precursor by a radical could result in secondary radicals being observed in the 1-butyl and isobutyl radical spectra, but no tertiary radical could be produced directly by hydrogen atom abstraction from the neopentyl radical precursor. Furthermore, there is no evidence of such reactions from the many studies which used organic nitrites to cleanly produce specific radicals[7,26,91]. No alternative nitrite decomposition pathways, which would be competitive with reactions 1 and 2 and lead to radical products, can be proposed. It has been reported that 1-butyl radical eliminates molecular hydrogen, presumably to form 1-methyl-allyl radical[96]. Isobutyl radical undergoing an analogous reaction would form 2-methylallyl radical. These decomposition pathways cannot explain the additional radical bands observed. The adiabatic IPs of these allylic radicals are 7.49 and 7.90 eV, respectively[90]. The band onsets are ~0.1 eV lower, but still too high to correspond to those observed for the low intensity bands appearing near the onset of the 1-butyl and isobutyl

radical photoelectron bands.

The primary benefit of these observations may be to suggest new experiments. If these reactions are unimolecular, they provide evidence, at high temperatures, for reactions previously thought not to be competitive with the decomposition reactions. If they are wall-catalyzed, they draw attention to possible complications in kinetic experiments involving these radicals.

Conclusion

Photoelectron spectroscopy is unique as an experimental technique for obtaining thermochemical and structural information about high-energy carbonium ion isomers. Analysis of the photoelectron spectra of 1-propyl, 1-butyl, isobutyl, neopentyl and 2-butyl radicals, combined with the heats of formation of the radicals, yields heats of formation of 1-propyl, 1-butyl, isobutyl, neopentyl and 2-butyl cations. An examination of the spectra presented here and the spectra of ethyl and 2-propyl radicals reported previously[7] reveals trends in ionization potentials which can be interpreted in terms of inductive and hyperconjugative effects of methyl substituents beta to a primary or secondary cation center.

The primary cation heats of formation have been discussed in light of theoretical calculations and energetics of cation rearrangements in solution which may involve primary cations as high-energy transition states or intermediates. The heat of formation of 2-butyl cation derived here is in good agreement with values obtained from appearance potential measurements and equilibrium constants for proton-transfer reactions. This agreement suggests that if classical 2-butyl cation does easily rearrange to a more stable hydrogen-bridged structure, the difference in

energy between the classical and rearranged structure is small. NMR experiments support this suggestion. Photoelectron data also yield the difference between the heats of formation of 2-butyl and tert-butyl cations. This value is in close agreement with that from solution calorimetric studies. This agreement, and the results of comparisons made between relative heats of formation of gas-phase cations and energetics of reactions in stable-ion media, support previous studies which indicate that differential solvent effects on cation isomers are small. There is some indication that solvation energies may decrease slightly in the order primary ion > secondary ion > tertiary ion.

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CHAPTER IV

Detection of Gas-Phase Organic Radicals Formed in Gas-Surface Reactions by Photoelectron Spectroscopy: Abstraction of Allylic Hydrogen by Bismuth Oxide

Detection of Gas-Phase Organic Radicals Formed in Gas-Surface Reactions by Photoelectron Spectroscopy: Abstraction of Allylic Hydrogen by Bismuth Oxide

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Abstract

Photoelectron spectroscopy has been used to detect gas-phase organic radicals as well as stable products formed in low-pressure gas-surface reactions. The products were sampled directly after exiting the catalyst bed. Allylic hydrogen abstraction by Bi_2O_3 at 760^{o} C forms gas-phase allyl and 2-methylallyl radicals from propylene and isobutylene, respectively, in the presence of oxygen. CO_2 and H_2O are the other observed products of alkene oxidation over Bi_2O_3. The product distributions and the 2-methylallyl radical yields as a function of oxygen pressure and Bi_2O_3 temperature are discussed.

Introduction

As an extension of our continuing efforts to obtain the photoelectron spectra of organic free radicals[1-5], we have investigated the possibility of monitoring by photoelectron spectroscopy gas-phase radicals produced by gas-surface reactions. Organic radicals escaping the surface of heated solid catalysts during gas-surface reactions have been detected by matrix isolation ESR spectroscopy[6,7], mass spectrometry[8], and matrix isolation IR spectroscopy[9], but not by photoelectron spectroscopy. Photoelectron spectroscopy has been used to analyze the stable products of heterogeneously catalyzed reactions[10], and to detect transient species other than organic radicals produced by flowing a gas over a solid reactant. For example, SiF_2 produced by flowing SiF_4 over heated Si has been detected by photoelectron spectroscopy[11]. Using photoelectron spectroscopy, stable and transient products of a low-pressure gas-surface reaction can be sampled directly after exiting the catalyst bed. Since organic radicals generally have lower ionization potentials than closed shell organics, photoelectron spectroscopy has a high selectivity for their detection. Furthermore, it has the ability to distinguish between isomers by their ionization potentials and photoelectron band shapes.

In the present study, bismuth oxide catalyst (Bi_2O_3) was chosen as the solid since it has been shown by Lunsford and coworkers using matrix isolation ESR spectroscopy to produce gas-phase allyl radicals upon interaction of propylene with its heated surface[6,7]. Interest in the catalytic properties of bismuth oxide comes primarily from a desire to understand its role as a component of bismuth molybdate catalysts used commercially for heterogeneous oxidation of propylene to acrolein.

The results of investigations into the mechanism of selective oxidation of propylene have been reviewed[12,13], and it is generally accepted that the rate-determining step in this catalytic reaction is the abstraction of an allylic hydrogen in propylene by lattice oxygen. Some experiments have been interpreted to indicate that the lattice oxygens involved in this step are associated with bismuth. Consistent with this, the major stable products of propylene over Bi_2O_3 are the radical coupling product, 1,5-hexadiene, and CO_2.

There are several advantages associated with the selection of allylic radicals for an initial investigation. The first band (adiabatic ionization potential = vertical ionization potential = 8.13 eV) of the allyl radical photoelectron spectrum has sharply resolved vibrational structure[1] and is therefore readily assigned. Several other resonance stabilized organic radicals, which could be produced by abstraction of a hydrogen atom next to a double bond, also have sharply structured first photoelectron bands[1,5,14]. Furthermore, allylic radicals are thermally stable and are not readily pyrolyzed.

Results

The photoelectron spectrometer used in this study is of standard design, modified to study the products of gas-phase pyrolysis[1]. The pyrolyzer consists of a 3 mm ID quartz tube, at one end of which a 2.5 cm length is wrapped with a noninductive heater. A thermocouple wedged between the heater and the quartz tube is used to monitor the temperature. Gases flow through the tube, traveling 0.75 cm after leaving the heated region and before intersecting the photon beam from the HeI lamp, where they

are ionized. The residence time of the gases in the heated region is on the order of 1 msec. For these experiments, the heated section of quartz tube has been filled with Bi_2O_3 chips (~1 mm x 1 mm x ½ mm size chips), a small amount of quartz wool at each end being used to keep the chips in place. The Bi_2O_3 chips were made by mixing Bi_2O_3 powder (Alfa Products, 99.8%) with water to form a thick paste, drying this in air up to a temperature of 650° C, and breaking the material into chips[6]. Before and after each set of experiments, the Bi_2O_3 chips were heated in flowing oxygen for at least one hour at 500° C. Spectra were analyzed by comparing them with spectra of reactants and possible products taken from the literature or recorded on our spectrometer using authentic samples.

At a temperature of 750° C and using a ratio of oxygen to propylene of 1 to 5 (total pressure in the catalyst bed is ~10^{-2} torr), ~1% allyl radical, relative to propylene, was observed[15,16]. No significant amounts (<5%) of acrolein[17] or 1,5-hexadiene (allyl radical recombination product) and no photoelectron band which could be assigned to the allyl peroxy radical ($C_3H_5O_2\cdot$)[18] were observed. A small amount of CO_2 was observed. A small amount of H_2O, the other product of complete oxidation of hydrocarbons, could also be present but was not detected due to overlapping O_2 and H_2O photoelectron spectra.

To investigate the generality of allylic hydrogen abstraction by Bi_2O_3, the products of isobutylene interacting with Bi_2O_3 were monitored. At a temperature of 760° C and using a ratio of oxygen to isobutylene of 1 to 5 (total pressure in the catalyst bed is ~10^{-2} torr), ~2% 2-methylallyl radical, relative to isobutylene, was observed[15,16]. Confirming our spectral assignment, photoelectron spectra of 2-methyl-

allyl radical from two different sources are shown in Figure 1. For the spectrum shown in Figure 1a, the radical was produced by the interaction of isobutylene with Bi_2O_3 under the experimental conditions described above. Figure 1b presents the spectrum obtained by pyrolysis of an appropriate alkyl nitrite precursor, part of a complete study of C_4H_7 radical photoelectron spectra[5]. No significant amounts (<5%) of methacrolein[19] or 2,4-dimethyl-1,5-hexadiene were observed when isobutylene and oxygen were passed over Bi_2O_3 at 750° C. No photoelectron band which could be assigned to 2-methylallyl peroxy radical[18] was observed. Small amounts of CO_2 and H_2O were observed.

The effect of varying the temperature of the catalyst on the production of 2-methylallyl radical was investigated (using a pressure ratio of oxygen to isobutylene of 1 to 5). The intensity of the 2-methylallyl radical spectrum, compared to the isobutylene He Iβ spectrum, monotonically increased over the temperature range 650 - 750° C. Temperatures higher than 750° were avoided because the melting point of Bi_2O_3 is 817° C. Below 650° C the 2-methylallyl radical band is too weak to quantify. The limited temperature range and low signal levels precluded a more quantitative analysis of the temperature dependence of radical yields. However, our results are consistent with an effective activation energy for radical production in the range of 10 to 35 kcal/mol.

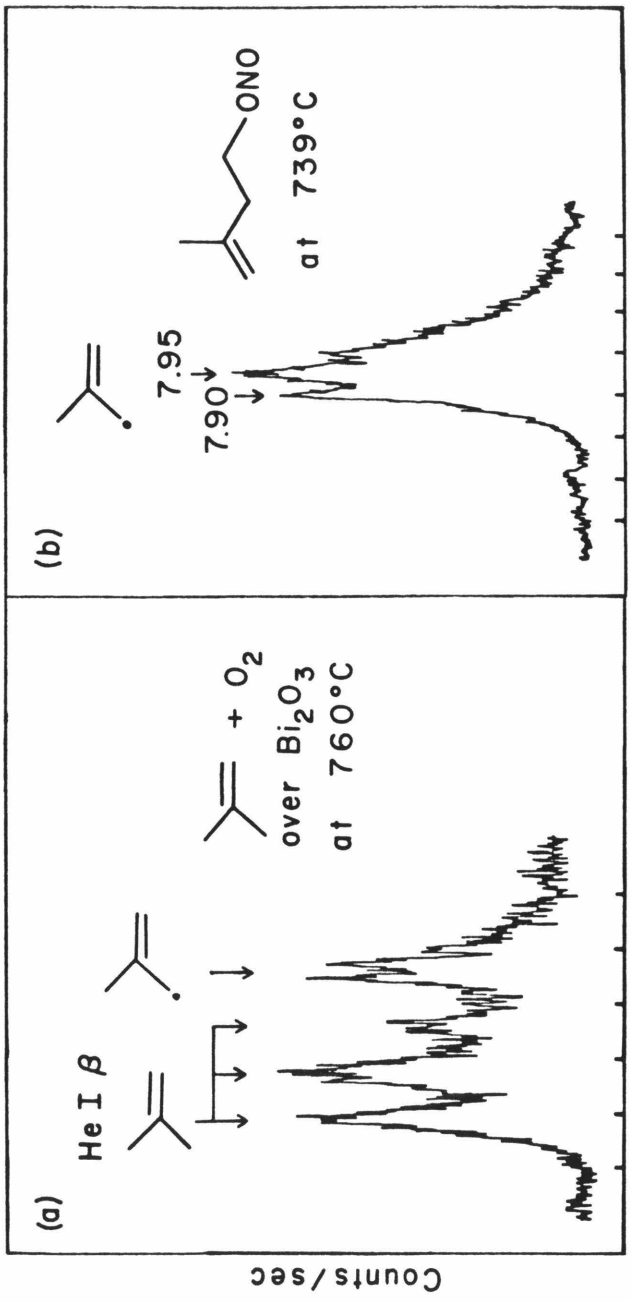
The effect of varying the oxygen to isobutylene pressure ratios on the production of 2-methylallyl radicals at 750° C was also investigated. The amount of 2-methylallyl radicals produced was constant for oxygen to isobutylene ratios between 1 to 4 and 1 to 8. Only with very low oxygen pressures (ratios less than ~1 to 100) was a marked decrease in

Figure 1. He I photoelectron spectra of 2-methylallyl radical which has been produced by

(a) the interaction of isobutylene with Bi_2O_3 at 760^{o} C in the presence of oxygen and

(b) the pyrolysis of 3-methyl-3-buten-1-yl nitrite (adapted from reference 5).

In addition to 2-methylallyl radical, the first photoelectron band of isobutylene ionized by the He Iβ line of the He I lamp[17] is observed in (a).


(a)
He I β
+ O2
over Bi2O3
at 760°C
(b)
7.95
7.90
ONO
at 739°C
Counts/sec
7.2
7.6
8.0
7.6
7.8
8.0
8.2
Ionization Potential (eV)

production of 2-methylallyl radicals observed. With no oxygen flowing, radical production was still observed.

No 2-methylallyl radicals were observed at 750° C when the catalyst and quartz wool were absent. To demonstrate that the Bi_2O_3 chips and quartz wool plugs do not simply increase the residence time of isobutylene in the heated region, thus allowing pyrolysis or gas-phase oxidation of isobutylene, the Bi_2O_3 chips were replaced with similarly sized quartz chips and the amount and configuration of the quantz wool were reproduced. No 2-methylallyl radicals were observed at 750° C using this experimental arrangement.

Discussion

Using photoelectron spectroscopy, we have been able to detect gas-phase organic radicals formed in gas-surface reactions. Allyl and 2-methylallyl radicals were formed by allylic hydrogen abstraction by Bi_2O_3 from propylene and isobutylene, respectively, in the presence of oxygen. CO_2 and H_2O are the other observed products of alkene oxidation over Bi_2O_3. In experiments where only stable products could be detected, 1,5-hexadiene and CO_2 were the major products of propylene oxidation over Bi_2O_3[12,13]. Martir and Lunsford concluded by comparison of allyl radical and 1,5-hexadiene concentrations over Bi_2O_3 that gas-phase radical recombination reactions served as a major pathway for the formation of 1,5-hexadiene[6]. With direct sampling of a low-pressure reaction region and a somewhat lower sensitivity for the detection of dienes than allylic radicals, it is not unexpected that we observed no diene production in our experiments.

The production of 2-methylallyl radical from isobutylene and oxygen flowing over Bi_2O_3 increases with the catalyst temperature, indicating its formation is an activated process. Lunsford and coworkers reported apparent activation energies of 14 [6] and 16.1 ± 1.6 [7] kcal/mol for the formation of allyl radical from propylene over Bi_2O_3. An activation energy of 22 kcal/mol has been reported for the reaction of propylene in the presence of oxygen to form 1,5-hexadiene over Bi_2O_3 [20] and values of 27.5 [21] and 29.0 [20] kcal/mol have been reported for the reaction of propylene with Bi_2O_3 in the absence of oxygen. Although a precise activation energy could not be extracted from our results for isobutylene over Bi_2O_3, the observed change in the intensity of the radical spectrum with temperature is consistent with an effective activation energy for the formation of 2-methylallyl radical in the range of 10 to 35 kcal/mol. Thus, our results for the temperature dependence of the allylic hydrogen abstraction by Bi_2O_3 from isobutylene are consistent with activation energies determined for the reaction of propylene over Bi_2O_3. This is not unexpected since the allylic C-H bond energies in propylene and isobutylene differ by only 1.6 kcal/mol [22].

The yield of 2-methylallyl radical decreases if the pressure of oxygen flowing with the isobutylene over the Bi_2O_3 is decreased to a very low level, although radicals are still observed with no oxygen flowing. Martir and Lunsford also observed a decrease in the yield of allyl radical production from propylene over Bi_2O_3 at very low levels of oxygen [6]. These results are consistent with Bi_2O_3 being an oxidant, in the absence of gas-phase oxygen, for the dehydrodimerization of propylene to form 1,5-hexadiene [21]. When gas-phase oxygen is present, it can replenish the lattice oxygens, regenerating the active site for hydrogen abstraction.

Thus, over the timescale of our experiments (1 to 2 hours), if the oxygen pressure is too low, the activity of the Bi_2O_3 decreases.

The importance of surface-initiated gas-phase reactions, in which gas-phase oxygen may participate, has been demonstrated under certain conditions for the oxidation of propylene over bismuth molybdate catalysts[12]. In the experiments of Martir and Lunsford[6], allyl radical production over Bi_2O_3 reached a maximum with a ratio of ~1 to 50 for oxygen to propylene. They explained the decrease at higher oxygen pressures as due to increased peroxy radical production via the association reaction of gas-phase allyl radical and oyxgen in the cooler postcatalytic volume. Our experimental arrangement allows us to sample the gases immediately after they leave the catalyst, and thus we observe no decreased radical production at higher oxygen pressures.

To further test the generality and selectivity of heated Bi_2O_3 to abstract allylic or other labile hydrogens and to form gas-phase radicals to be detected by photoelectron spectroscopy, we have examined briefly the reactions of other organic molecules over Bi_2O_3 in the presence of oxygen. Although the energetics of forming benzyl radicals, which have an adiabatic and vertical ionization potential of 7.20 eV[1], are favorable, none were detected (<1%) when toluene was passed over Bi_2O_3 at 760° C. Cycloheptatriene produced at 760° C ~2% tropyl radicals, which have an adiabatic ionization potential of 6.28 eV[14]. The major reaction observed, however, was the isomerization of approximately half the cycloheptatriene to toluene. CO_2 and H_2O were also produced. A significant fraction of trimethylsilane was oxidized to H_2O and CO_2 at 625° C. No trimethylsilyl radicals, for which an estimated ionization potential is 6.30 eV[23], were observed. Trimethylamine produced no (<1%) dimethylaminomethyl radicals

($(CH_3)_2NCH_2$) at 760° C. An estimated ionization potential for this radical is 5.7 eV[24]. In an effort to obtain the photoelectron spectrum of cyclopentadienyl radical, cyclopentadiene and oxygen were passed over heated Bi_2O_3. At 550° C large amounts of CO_2 and H_2O were formed in addition to a product whose first photoelectron band has an adiabatic and vertical ionization potential coinciding at 8.16 ± .03 eV. Two other bands in the photoelectron spectrum of the products of cyclopentadiene over Bi_2O_3, with vertical ionization potentials of 9.0 and 11.2 eV, have intensities that remain proportional to the band at 8.16 eV as the catalyst temperature is varied and therefore may arise from the same reaction product. We have not been able to assign this spectrum. The ionization potential is lower than 8.41 eV, the value determined for cyclopentadienyl radical by Lossing and Traeger using an electron monochromator-mass spectrometer combination[25]. Although dimerization products were not observed in the reactions of alkenes, this possibility must be considered in view of the fact that Bi_2O_3 is more reactive towards cyclopentadiene. In this system the production of a large amount of cyclopentadienyl radicals may occur and result in the formation of dimerization products. However, the unidentified band cannot be due to the radical recombination product since it has an ionization potential of 7.75 eV[26]. Perhaps dimerization and then dehydrogenation could occur to form fulvalene. No experimental value for the ionization potential of this transient species is available. Napthalene, the stable isomer of fulvalene, is ruled out by a comparison of the photoelectron spectrum of this species to that observed in the present work. The spectrum cannot be assigned to cyclopentadienone, a possible oxidation product of cyclopentadiene, which has a first vertical ionization potential of 9.41 eV[27]. We are continuing our efforts to obtain the photoelectron spectrum of cyclopentadienyl radical using other radical sources.

Other catalysts can also be tested for their ability to produce gas-phase organic and inorganic radicals[28]. These studies may provide information about the gas-surface reactions as well as lead to means of producing radicals not yet observed by photoelectron spectroscopy and thus allow their spectrum to be obtained. Photoelectron spectroscopy has been used extensively to optimize desired stable products of gas-phase reactions with heterogeneous catalysts[10]. As shown in this work, photoelectron spectroscopy may be used to sample directly both the transient and stable products of gas-surface processes.

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15. Relative concentrations of allylic radical and alkene were estimated by comparing the intensity of their He Iα first photoelectron bands

(counts/sec at their maxima). This was accomplished by directly comparing the He Iα first photoelectron band of the radical and the He Iβ first photoelectron band of the alkene. The relative intensity (3:100) of the He Iβ to the He Iα band is then taken into account. Since absolute cross sections are not known, this method was chosen for its convenience and should yield a value within a factor of five of the actual relative concentration.

16. The major line of the He I lamp, He Iα, is at 21.22 eV and an impurity line, He Iβ, is at 23.09 eV with a relative intensity to He Iα of 3:100. Electrons ionized by the He Iα line have 1.87 eV higher kinetic energy than those ionized by He Iα and therefore appear in the He I spectrum at lower ionization potential by 1.87 eV from the major He Iα bands.

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